A-447

GEORGIA INSTITUTE OF TECHNOLOGY
Engineering Experiment Station
Atlanta, Georgia

MECHANISM OF THE PHASE TRANSITIONS IN QUARTZ

Technical Operating Report No. 1

Period Covered: April 1, 1959 - June 30, 1959

Contract No. AF 49(638)-624
(Project A-447)

July 1, 1959

R. A. Young
Project Director

Air Force Office of Scientific Research
Washington 25, D. C.

Technical Operating Report No. 1, Project No. A-447

I. Title

Mechanism of the Phase Transitions in Quartz

II. Objective and Scope

The purpose of this project is to make a definitive study, by x-ray means, of the $\alpha \rightleftarrows \beta$ transition in quartz. Data will necessarily be collected at controlled temperatures near the transition temperature, 573°C. Electron density maps will be prepared corresponding to temperatures near the transition temperature. The intensity of selected reflections will be followed as a function of temperature near and, if possible, through the transition temperature. The information so obtained is expected to allow a detailed, quantitative discussion of the phase transition in terms of both the changes in the thermal vibrations and the changes in the equilibrium positions of the atoms.

III. Current Status

Different quartz specimens are known to show slightly different transition temperatures and hysteresis characteristics. Therefore, a variety of specimens should be included in the study. At the suggestion of Mr. Max Swerdlow of OSR, access was requested and granted to the quartz collections of Dr. Tuttle (actually Professor MacKenzie Keith) at the Pennsylvania State University and Dr. Earl Ingerson at the University of Texas. Dr. Vernon Hurst, Georgia State Department of Mines, has also provided some specimens. Dr. R. A. Laudise of Bell Telephone Labs will furnish synthetic specimens including, if desired, a range of doping. Thus sources of a sufficiently wide variety of specimens are assured.

On the suggestion of Mr. Swerdlow the principal investigator has visited, discussed his program with, and solicited comments from Dr. Hatten Yoder (Geophysical Laboratory), Dr. Ray Walker (NBS), and Dr. H. McMurdie (NBS). Dr. Yoder was particularly helpful and was interested in the intended technique more than in the particular transition. He suggests that the technique might fruitfully be applied to the K_2SO_4 or the Na_3AlF_6

(cryolite) transition or to studies of melting mechanisms. Suggestions were received from both Dr. Walker and Dr. Yoder concerning heating rates, heating devices and temperature control needed.

Initiation of experimental work has been greatly hampered by a lack of personnel. The lack was occasioned by an unexpected influx of research contracts to the Physics Branch. It has been corrected only during the last week of this quarter when an additional research assistant became available. Mr. R. A. Langley started working with us about 5 hours per week as a student assistant during the quarter. Upon graduation June 13, he became a graduate research assistant (graduate student in physics). Since then, he has received a National Defense Education Act scholarship. It was intended that he should be the graduate student mentioned in the original proposal for this work. His receipt of the scholarship means that the graduate student position will be vacated in September. Some delay may be encountered in refilling that position. The lack of personnel during the first quarter of this project will almost surely occasion a request for an extension of the contract period at no additional cost.

The little personnel time that has been available for experimental work has been spent on design and construction of the hot-air furnace which is initially to be tried for heating the specimens by blowing hot air on them. No satisfactory model has yet been constructed. A "uniform" temperature over a large enough cross section of the hot-air stream has not yet been achieved. Work continues on the furnace.

IV. Plans for Future Work

It is expected that the hot-air furnace will be completed satisfactorily early in the next quarter, that suitable means for mounting the shaped crystal specimens will be found quickly, and that data collection will be started. It is expected that film methods (mostly precession) will be used for general survey work and counter methods will be used to obtain detailed quantitative information. Both film and counter methods are currently in use in the laboratory for other unrelated, single-crystal studies.

Respectfully submitted,

Approved:

R. A. Young
Project Director

Vernon Crawford
Head, Physics Branch
Physical Sciences Division

A-447

GEORGIA INSTITUTE OF TECHNOLOGY
Engineering Experiment Station
Atlanta, Georgia

MECHANISM OF THE PHASE TRANSITIONS IN QUARTZ

Technical Operating Report No. 2

Period Covered: July 1, 1959 - September 30, 1959

Contract No. AF 49(638)-624
(Project A-447)

October 1, 1959

R. A. Young
Project Director

Air Force Office of Scientific Research
Washington 25, D. C.

I. TITLE

Mechanism of the Phase Transitions in Quartz

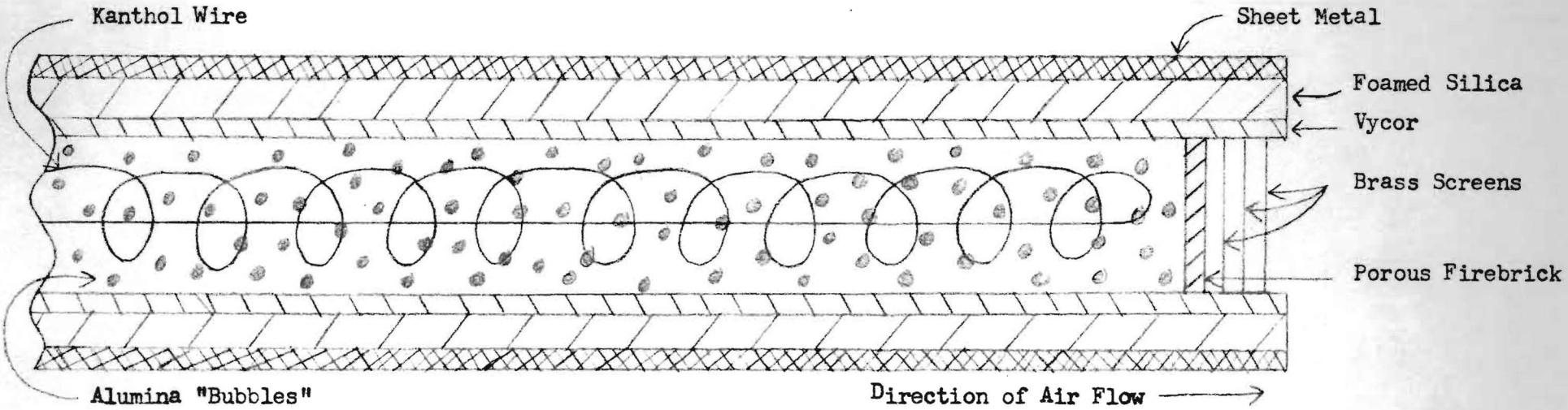
II. OBJECTIVE AND SCOPE

The purpose of this project is to make a definitive study, by x-ray means, of the $\alpha \rightleftarrows \beta$ transition in quartz. Data will necessarily be collected at controlled temperatures near the transition temperature, 573°C. Electron density maps will be prepared corresponding to temperatures near the transition temperature. The intensity of selected reflections will be followed as a function of temperature near and, if possible, through the transition temperature. The information so obtained is expected to allow a detailed, quantitative discussion of the phase transition in terms of both the changes in the thermal vibrations and the changes in the equilibrium positions of the atoms.

III. CURRENT STATUS

The Furnace

Design. A furnace has now been constructed which appears to perform satisfactorily. It consists principally of a 40 centimeter length of 18 mm Vycor tubing containing a heating coil made of Kanthol wire packed in irregularly shaped chips of zirconia. The outlet end is closed with a porous firebrick plug to prevent the zirconia from blowing out when air is passed through the unit. Three layers of 100 mesh-brass screen just inside the mouth of the tube considerably reduces the temperature gradients across the central portion of the outlet air stream. The whole tube is surrounded by an insulating jacket made of foamed silica and by a protective jacket of sheet metal. The relationship of these various parts is shown in Figure 1. A chromel-alumel thermocouple, made of 3 mil diameter wire, is permanently fastened across the outlet (with the junction centered in the outlet) with Sauereisen cement. The outside diameter of the device is about 4 centimeters. The inside and outside diameters used here represent compromises among the requirements of (1) a large inside diameter to reduce the lateral temperature gradient at the center of the hot air stream, (2) a small outside



HOT AIR FURNACE

Figure 1

diameter in order to allow positioning of the furnace to heat specimens on the precession camera or the counter-adapted Weissenberg, and (3) enough insulation to prevent significant lateral heat losses from the furnace (which would have the effect of increasing the transverse temperature gradients in the hot air stream).

Performance. With an input of 10 amps at 110 volts to the heater coil the exit temperature is about 740°C with an exit flow velocity on the order of 2 cubic feet per minute. Both the transverse and longitudinal temperature distribution in the exit air stream have been investigated both with bare thermocouple junctions and with thermocouple junctions on which quartz crystal specimens, of the size and shape which we will be examining, have been mounted. At one centimeter away from the end of the tube there is a roughly circular 5 mm diameter region over which the temperature indicated by the thermocouple does not vary by more than $\pm$ 5°C (at 740°C). This approximation to a uniform temperature distribution in the hot air stream should make it possible to reproduce the specimen temperature to within one or two degrees C, particularly if regular checks are made by substituting a thermocouple at the specimen position.

Mounting. A minor problem arises with respect to mounting the hot air furnace to heat specimens on the precession camera. It was felt that it was undesirable to have the furnace mounted on any of the moving parts of the camera. In order to mount the furnace in a stationary position and yet allow a full 30° precession angle the hot air blast must be directed at some part of the camera in such a direction that a portion of the photographic film will move through it when the camera is in operation. It is expected that suitable baffles can be constructed, probably from nickel foil, to deflect the hot air stream and prevent damage to the camera or film. Perhaps a separate stream of room temperature air will be directed onto the back surface of this baffle.

Samples

Preparation and mounting. A number of specimens of Georgia and of Brazilian quartz have been ground in the sphere grinder until they have

assumed an ellipsoidal form in which the major dimension is in the range 0.8 to 0.2 mm. Some of the specimens are nearly spherical; further grinding will be done. It is expected that the grinding technique currently being used will be satisfactory for the purposes of this project.

Prior to final mounting of specimens, orientation procedures have been carried out both optically and by x-rays. Two optical methods have been used: (1) the usual method of finding optic axes with a petrographic microscope and (2) a technique which involves mounting the "spherical" specimen at random (on the end of a glass fiber), the use of simple polarizing optics added to the precession camera, and the possible re-mounting one or more times until a suitable orientation is obtained. The trial mountings, which are made during the orientation procedures whether done by optics or by x-rays, are made with one of a pair of adhesives each of which is insoluble in the other's solvent. The final mounting is made on a quartz fiber with a heat resistant cement. We are currently using Sauereisen No. 1. This material seems to maintain a satisfactory bond both to the crystal and the fiber over the temperature range required. A disadvantage is that special care must be taken in order to get a good bond in the first place. Gentle heating seems to be required; too strong heating results in a sudden expansion of the Sauereisen which may envelop the crystal; without heating a bond strong enough to maintain the orientation of the crystal upon subsequent transfer to other locations seems not to be formed every time even though drying times of several hours are allowed. Other adhesives will be tried as they come to our attention.

Behavior on heating. Two different "spherical" quartz specimens have been heated through the transition temperature, while held in place by the Sauereisen cement, and cooled again with no apparent damage. The particular crystal which was fastened to the end of the thermocouple and was used for investigating the temperature distribution in the air stream from the furnace has now passed through the transition temperature at least a dozen times and appears still to be intact. Furthermore, since this crystal has been rather abruptly thrust in and out of the hot stream, we apparently may anticipate no trouble from our small specimens breaking up on going through the transition.

Training

Because some of the people involved in this project are quite inexperienced, it has been, and will continue to be, necessary to give some direct attention to the training of persons associated with the project. This training includes techniques for grinding and mounting the crystals, for orienting the crystals both optically and by x-ray methods, and for the use of the precession camera and other equipment. Beyond and more important than the manipulatory training is the need for training in such things as the concept of the reciprocal lattice and the Ewald sphere, familiarization with the quartz structure, and in general the principles and techniques of investigating structural details by x-ray diffraction. The attempt is made, in this training, to stress, insofar as is possible and is consistent with the purposes of the project, the theoretical background of all that is done and might be done. A considerable portion of the principal investigator's time during the past quarter has necessarily been devoted to this training function. After only spending half time for three months with us (as a graduate research assistant), Mr. Langley has left us because he was fortunate enough to get a substantial scholarship which prohibits him from undertaking paid employment.

While the training efforts expended on him are lost insofar as the immediate goals of this particular project are concerned, it is believed that in view of the avowed interest of OSR in training graduate students and in stimulating their interests, the efforts are by no means wasted; Mr. Langley has apparently been sufficiently impressed by the training he received while with us that he is contemplating doing his graduate thesis with us on some other x-ray problem.

IV. PLANS FOR FUTURE WORK

It is expected that during the next quarter a series of precession pictures will be obtained at temperatures both above and below the transition temperature of quartz. It is expected that these precession pictures will help to point out which reflections should be studied in most detail, by counter methods, over a temperature range which includes the transition

temperature. If a particular reflection can be found whose intensity changes markedly at the transition temperature it will be useful for temperature calibration. It is expected that some counter data will also be obtained during the next quarter.

V. PERSONNEL

Mr. R. A. Langley, graduate research assistant (Physics), left the project as of September 21 to accept a National Defense Education Act scholarship which prohibits his further employment. No replacement for him has yet been found. Miss Roxana Speight, BS in mathematics from Agnes Scott College, June, 1959, joined the x-ray laboratory in June. In September she started devoting part of her time to this project. It is expected that she will devote approximately one-half time to it in the future.

VI. BUDGETARY MATTERS

Approximately $3000 has been expended during the present quarter. There are about $35,500 and 18 months of the contract period remaining.

VII. MISCELLANEOUS

The principal investigator presented a paper entitled "Electron Density and Thermal Effects in Quartz," of which Dr. Ben Post of the Polytechnic Institute of Brooklyn was co-author, at the annual meeting of the American Crystallographic Association, July 19-24, 1959, at Cornell University. While none of the work presented in that paper was supported by this project, it is mentioned here because it is highly relevant to the present study.

Respectfully submitted,

R. A. Young
Project Director

Approved:

Vernon Crawford
Head, Physics Branch
Physical Sciences Division

A-447

GEORGIA INSTITUTE OF TECHNOLOGY
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MECHANISM OF THE PHASE TRANSITIONS IN QUARTZ

Technical Operating Report No. 3

Period Covered: October 1, 1959 - December 30, 1959

Contract No. AF 49(638)-624
(Project A-447)

January 1, 1960

R. A. Young
Project Director

Air Force Office of Scientific Research
Washington 25, D. C.

Technical Operating Report No. 3, Project No. A-447

I. TITLE

Mechanism of the Phase Transitions in Quartz

II. OBJECTIVE AND SCOPE

The purpose of this project is to make a definitive study, by x-ray means, of the $\alpha \leftrightarrows \beta$ transition in quartz. Data will necessarily be collected at controlled temperatures near the transition temperature, 573°C. Electron density maps will be prepared corresponding to temperatures near the transition temperature. The intensity of selected reflections will be followed as a function of temperature near and, if possible, through the transition temperature. The information so obtained is expected to allow a detailed, quantitative discussion of the phase transition in terms of both the changes in the thermal vibrations and the changes in the equilibrium positions of the atoms.

III. CURRENT STATUS

Both film and counter data have been collected which, while still very few and quite preliminary, are very promising.

The Furnace and its mounting

The problem mentioned in the last report, that of mounting the furnace on the precession camera, was easily solved. The hot-air-stream furnace, essentially as described in the last report, has been used both with and without automatic temperature control and appears to perform satisfactorily.

X-ray data and observations

With the furnace operated on automatic temperature control precession pictures in the $(h0\ell)$ zone were obtained at temperatures both above and below the transition temperature. An $\alpha \leftrightarrows \beta$ phase transition effect which was clearly shown by these pictures was that of making the $(h0\ell)$ reflections equivalent to the $(\bar{h}0\ell)$. The particular reflections which showed the greatest change, the $\{301\}$ reflections, are being examined with a counter technique. For these examinations the crystal is mounted on a Wissenberg camera which has been adapted to the use of a scintillation counter instead of film. The same hot-air-stream furnace is used for heating the specimens in this arrangement. Although the studies with the counter have just begun,

and have so far been confined to only one reflection type from one specimen, several very interesting observations have been made:

(1) While the diffracted intensities of both the (301) and the ($\bar{3}$01) change continuously from room temperature to the transition temperature, they both show abrupt and apparently at least nearly discontinuous changes at the transition. This shows that at the transition there is an abrupt change in either the positions or the thermal motions (or both) of the atoms. The actual experimental observation of the transition's effect on (301) is somewhat spectacular. With counter and crystal positions fixed and the intensity being continuously recorded, the onset of the transition is announced by the noise of the recorder motor as it is suddenly required to drive the pen up or down the scale by 50 to 100% of the initial deflection.

(2) The intensity changes in the (301) reflections from room temperature to the transition temperature are not monotonic. This suggests that both atomic positions and thermal motions change with temperature changes over this range.

(3) The three equivalent directions in the α - form may be chosen from the six equivalent directions in the β - form in either of two ways. On going from α to β and back to α it often happens that the possibility alternate to that initially existing has occured! This is equivalent to having rotated the crystallographic axes by 60° without having rotated the mass of which the crystal is composed. Among other things, this certainly shows unequivocally, and independently of intensity measurement of the β -form reflections, that the β -form has 6-fold symmetry.

(4) Room temperature diffracted intensities before and after the transitions appear to reproduce within experimental error. This means that the initially single, untwinned crystal has remained single in spite of having been transformed back and forth to the β -form and to the alternate α -form several times.

(5) It appears that we may control the choice of alternate α -forms resulting from the $\beta \rightarrow \alpha$ transition by the physical rotational position

of the specimens at the time. We suspect that the driving force for the choice may be the (probably small) thermal gradients due to the heating method.

Specimens

The specimen used for the above observations was Brazilian quartz. This and other specimens of Brazilian and other quartz materials have been and will be ground and mounted in the manner described in Technical Operating Report No. 2.

Training

The need for training, discussed in Technical Operating Report No. 2, continues (and will continue) to require a significant fraction of the principal investigator's time. However, as was pointed out before, it is felt that such expenditures of time as have been and likely will be made this way constitute an investment which will give good returns within the life of the project.

IV. PLANS FOR FUTURE WORK

During the next quarter the counter measurements of the temperature dependences of diffracted intensities through the transition temperature will be continued. They will be extended to other reflections and to other specimens. Some additional film data will probably be gathered with the precession camera. When we have obtained counter measurements of the temperature dependence of all observable (h0ℓ) intensities from room temperature through the transition temperature some Fourier syntheses (probably mostly Patterson diagrams) will be prepared.

V. PERSONNEL

As has been pointed out in the past, some difficulty has been experienced in staffing this project. However, it now appears that by February 1960 it will be possible to bring the rate of effort up to the initially proposed level.

Mr. Jude Koenig, B.S. in Physics in 1957 from Rockhurst College in Kansas City, joined the laboratory staff in December 1959 as an Assistant

Research Physicist. Mr. Koenig has three (3) years experience in industrial applications of x-ray diffraction. He will devote about one half time to the project. He seems very glad of the opportunity to engage in academic research. His enthusiasm and energy plus his experience with manipulation of x-ray diffraction equipment will make him quite valuable to the project.

An additional man with a B.S. in physics plus some graduate work at Tulane is expected to join the laboratory staff in January and to take graduate work at Georgia Tech. He will spend about one half time on the project and will complete the complement of permanently assigned technical persons required for the work of the project.

VI. BUDGETARY MATTERS

Approximately $1200 have been expended during the present quarter. (The principal investigator's time is not charged to the project during the academic year). There are about $34,500 and 15 months of the project period remaining. With the addition of the personnel mentioned it is anticipated that the expenditure rate will be sharply increased in the next quarter.

Respectfully submitted,

R. A. Young
Project Director

Approved:

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MECHANISM OF THE PHASE TRANSITIONS IN QUARTZ

Technical Operating Report No. 4

Period Covered: 1 January 1960 through 31 March 1960

Contract No. AF 49(638)-624
(Project A-447)

April 11, 1960

R. A. Young
Project Director

Air Force Office of Scientific Research
Washington 25, D. C.

GEORGIA INSTITUTE OF TECHNOLOGY
Engineering Experiment Station
Atlanta, Georgia

MECHANISM OF THE PHASE TRANSITIONS IN QUARTZ

Technical Operating Report No. 4

Period Covered: 1 January 1960 through 31 March 1960

Contract No. AF 49(638)-624
(Project A-447)

April 11, 1960

R. A. Young
Project Director

Air Force Office of Scientific Research
Washington 25, D. C.

Technical Operating Report No. 4, Project No. A-447

I. TITLE

Mechanism of the Phase Transitions in Quartz

II. OBJECTIVE AND SCOPE

The purpose of this project is to make a definitive study, by x-ray means, of the $\alpha \overleftrightarrow{\rightarrow} \beta$ transition in quartz. Data will necessarily be collected at controlled temperatures near the transition temperature, 573°C. Electron density maps will be prepared corresponding to temperatures near the transition temperature. The intensity of selected reflections will be followed as a function of temperature near and, if possible, through the transition temperature. The information so obtained is expected to allow a detailed, quantitative discussion of the phase transition in terms of both the changes in the thermal vibrations and the changes in the equilibrium positions of the atoms.

III. CURRENT STATUS

Additional preliminary data gathered and observations made during the quarter showed (1) interesting points of character in the temperature dependences of various reflections, (2) that certain minor modifications of the equipment were desirable, and (3) that the preliminary phase of the work is nearly at an end so the need for machine computation will soon arise. These points and others are discussed in more detail below.

Training

As was mentioned in Technical Operating Report # 2 a considerable amount of training of project personnel is necessary both in the general theory and practice of x-ray diffraction and in the specific aspects most relevant to the immediate work. A very simple example of a specific manipulative skill that must be acquired is that needed for mounting the small (< 0.3 mm diameter) spherical crystals on the ends of quartz fibers within

2 or 3 degrees of the desired orientation. The procedure used actually entails remounting by transferring a specimen from fiber to fiber one or more times. Since the precession camera is used to determine the crystal orientations (and hence the changes required in re-mounting) it is clear that even the seemingly elementary task of properly mounting the specimens requires some special knowledge and skill that new project personnel would be unlikely to have. Three people (Speight, Koenig, and Battson) have now acquired this and various other relevant skills and are making satisfactory progress in their continuing training. Mr. Battson, in particular, is also familiarizing himself with our computing needs and available computing programs and facilities.

Equipment Additions and Modifications

Experience gained in collecting preliminary x-ray intensity data up to and through the transition has led to several small modifications of the equipment. These include the incorporation of an x-y recorder into the circuits (to give a direct plot of intensity vs temperature), the addition of a much more sensitive null-indicator for use in making thermocouple emf readings, provision for cooling the scintillation counter, a start on a fine-positioning device to help explore more carefully the temperature distribution in the neighborhood of the crystal, and a new mounting of the furnace. The new furnace mounting and baffle arrangement allow exploration of the entire zero layer with no readjustment of furnace or baffle and with no obstruction of the x-ray beams. At the same time the specimen is closer to the mouth of the furnace than it was in the previous arrangement. A paper describing the counter attachment and this furnace design and arrangement is being offered for presentation at the 9th Annual "Denver Conference" on x-ray analysis, August 10, 11, 12, 1960.

Excepting for the efforts of the principal investigator during the academic year, the work on the furnace and its mounting was supported by

project funds; the design and construction of the counter adaptor were not. A copy of the abstract of the offered paper is appended.

Data and Observations

Several specific points concerning the various data and observations made during the quarter are mentioned below.

1. A general rise in the apparent intensity of the (301) reflection from about 400°C to the transition temperature was mentioned in the last report. The apparent rise was found to be caused by heating of the scintillation counter. An aluminum-foil shield was successful in keeping the counter cool. The general rise was thereby eliminated.

2. The intensity versus temperature curves seem to be wholly reversible in detail, even through the phase transition region, if slow enough heating and cooling rates are used.

3. It was pointed out in the last report (Technical Operating Report # 3) that the quartz crystal did not seem to become twinned even though it had been passed through the $\alpha \leftrightarrows \beta$ transition many times. Dauphine twinning might have been expected. A single instance of twinning has now been observed. It manifested itself in 2 ways: (a) The room temperature $(301)/(30\bar{1})$ intensity ratio was about 2 whereas for the untwinned crystal it is about 8. (b) The appearance of the intensity vs temperature curve was detectably modified.

In these circumstances Dauphine twinning represents opposite choices of the two alternate ways of extracting the 3 equivalent directions of the α-form from the 6 equivalent directions of the β-form. The twin was produced by rapid cooling (of the order of several tens to a few hundred degrees per minute) through the transition. On reheating and cooling more slowly the crystal was made single again. Deliberate production of twins and careful determination of the temperature at which the twins anneal out

may give information about the maximum temperature gradient in the specimen during the usual heating and cooling procedures.

4. It is possible, especially with the help of the better null-indicator, to show interesting, unexpected, and reproducible character in the intensity vs temperature curves in the immediate neighborhood of the transition. In the last few degrees below the transition, for example, the (301), (100), and (200) have been observed to show an increase in intensity followed by a decrease at the transition. Of the few reflections that have so far been this carefully followed, the (100) seems especially interesting. Its behavior is indicated qualitatively in Figure 1. It seems unlikely that an intermediate phase is indicated by this behavior; more probably it is due to marked changes in the character of the thermal vibrations. It is expected that this point will be resolved and that the nature and extent of the thermal vibration changes will be determined in the course of the present work.

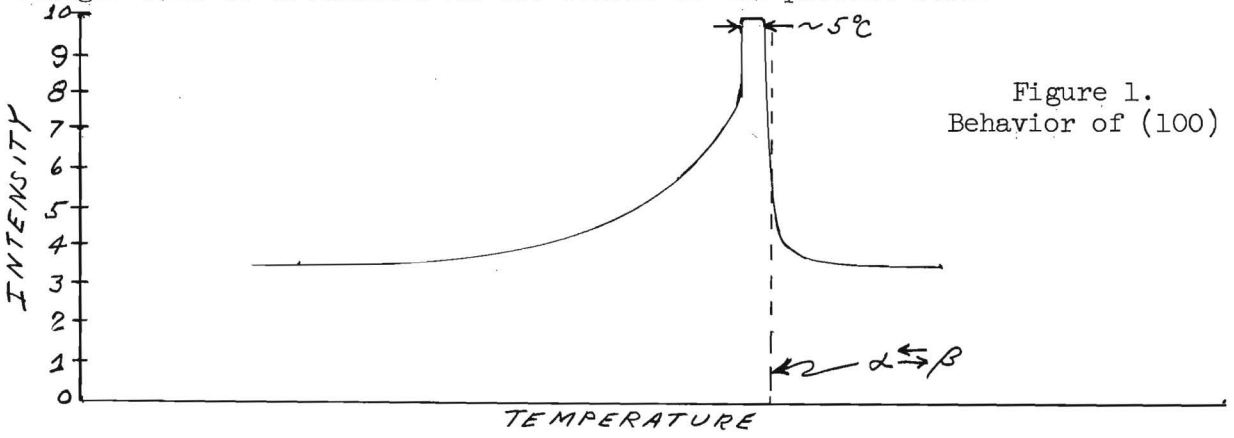

Figure 1.
Behavior of (100)

5. The various reflections do not show different transition temperatures. While this was expected it was felt that the fact should be demonstrated. The temperature was stabilized at a point which, as judged by the (100) intensity, was mid-way in the transition. Checking the (301) intensity showed that this reflection, too, indicated that the transition was arrested at approximately mid-way. The minimum transition temperature difference that could have been detected this way is estimated to be $2\frac{1}{2}^{\circ}C$. Repetition of this experiment with the use of the improved null-indicator will allow detection of a minimum difference of about $0.5^{\circ}C$.

6. A start has been made on gathering (h0ℓ) data at fixed elevated temperatures. Many more data at several temperatures will be gathered before any interpretations are attempted.

Preparation for Computing Needs

Four specific needs for high-speed machine computation are now recognized.

(1) Calculated values of a variety of structure factors, and hence intensities, are needed as a function of atomic coordinates and thermal ellipsoids so that the results of hypotheses concerning the temperature dependence of the magnitudes and character of the various thermal motions may be compared with experiment (by observations of intensity versus temperature) for selected reflections.

(2) A least squares, or equivalent, refinement procedure is needed in order to determine atomic coordinates and temperature factors, at each of several temperatures, by refinements based on isothermal intensity data collected at each temperature. The procedure should be followed by routines for converting the temperature factors to thermal ellipsoids, for determining bond lengths and angles from the coordinate results, and for determining the standard deviations.

The routines must handle individual anisotropic temperature factors for this acentric case.

(3) A two dimensional Fourier synthesis routine will be required for the preparation of Patterson diagrams and projected electron density maps.

(4) A three-dimensional Fourier synthesis routine may be required in order to compute sections of electron density and Patterson distributions.

Specific plans have been or are now being made to fill all of these needs except the last. The following steps have been taken:

(1) Negotiations are now in progress with the OSR Contract Office and with the National Bureau of Standards to make use of the IBM 704 machine and computer group at NBS. Dr. W. R. Busing's least squares routine and ancillary procedures have been successfully used on that machine. The principal investigator has previously benefited from results obtained with a closely similar program written by Dr. Busing and used by him on the ORACLE computer at Oak Ridge. Dr. Busing's program meets all of the requirements set forth in needs (1) and (2) above.

(2) In the Georgia Tech Computer Center there are a Datatron 220, an IBM 650, and a Univac Scientific 1101 computer. Need (3) above is probably adequately met by an existing program previously successfully used by the principal investigator on the Georgia Tech IBM 650 machine. The possibility that need (1) above can be met by modification of or simple additions to existing routines for the IBM 650 or Datatron 220 computer is being investigated. It is especially desirable to meet need (1) locally if possible.

Specimen Preparation

A continuing activity is that of grinding specimens to size and mounting them on quartz fibers in a predetermined orientation.

IV. Plans for Future Work

The training aspect of the work will necessarily continue for some time.

The temperature distribution in the hot air stream around the crystal will be further determined, with an especially small thermocouple, to within about $2^{\circ}C$. The transition temperatures of the Brazilian and the Georgia quartz specimens on hand will be compared. If they are closely similar, as is expected, then the following program of data collection will probably be undertaken:

(a) Intensities of the $\{h0\ell\}$ reflections at room temperature, $550^{\circ}C$, and $600^{\circ}C$ will be gathered first.

(b) During the process of collecting the data of (a), above, the intensities of several reflections will be followed through the transition temperature and a few will be followed from room temperature to $600^{\circ}C$ or above.

(c) Certain reflections, chosen on the basis of the first results and computations, will be followed in more detail.

(d) Three dimensional data will be gathered at two temperatures (or more).

(e) $\{h0\ell\}$ data may be gathered at additional temperatures.

(f) Spot checks will be made of the temperature dependences of the reflections from crystals of several different origins to see if there are differences among them which would indicate significant differences in the phase transition mechanism. (This will not be left entirely to such a late position in the program.)

Further equipment modifications may be undertaken. For example, a better potentiometer may be useful in determining the details of the temperature dependence of intensities over small ranges near the transition temperature. Ways of improving the effectiveness or efficiency of operations are always in demand.

It is expected that during the next quarter some high-speed-computer means for calculating expected intensities as a function of atomic coordinates and thermal ellipsoids will become available and that some calculations will be made and compared with experiments.

It will be especially interesting to try to check an hypothesis to the effect that the silicon atom (for example) in the β-form vibrates between its two possible α-form positions. When $\{h0\ell\}$ zone data are available for several temperatures one may check, in part, the hypothesis by noting the temperature dependence of the silicon coordinate. It may also be possible to do some checking sooner by comparing observed $\alpha \overset{\leftarrow}{\rightarrow} \beta$ intensity changes with those calculated for certain models based on this and other hypotheses.

V. Personnel

Mr. Donald F. Battson joined the laboratory in January, 1960. He will continue to devote the major portion of his time to this project. Mr. Battson holds a B.S. in Physics from Tulane and took about one year of graduate work in physics there. It is expected that he will soon continue his graduate studies here. No other changes have been made in the project personnel complement.

VI. Budgeting Matters

Approximately $4,000 have been expended during the quarter. (The principal investigator's time is not charged to the project during the academic year.) There are about $30,500 and 12 months of the project period remaining. It is planned that a no-cost extension, first mentioned in Technical Operating Report # 1, will be requested in the near future.

Respectfully submitted

R. A. Young
Project Director

Approved:

Vernon Crawford, Head
Physics Branch, Physical Sciences Division

Counter Adaptor and Furnace for Weissenberg Camera*

R. A. Young

Engineering Experiment Station
Georgia Institute of Technology
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A rugged and versatile counter-adaptor for a Weissenberg camera is described. It has performed well in two years of daily use which has included collection of intensity versus temperature data with conventional cold stream techniques.

Advantage has recently been taken of the adaptor design to mount, directly on the Weissenberg base, a furnace device which blows hot air along the crystal mounting axis. Crystal temperature may be held constant or easily varied over the range up to about 700°C, with no obstruction of the x-ray beams and no readjustment of the furnace position, while the entire zero layer and close-in upper layers are explored.

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* Work Supported in Part by the Air Force Office of Scientific Research, Contract No. AF 49(638)-624.

Offered for presentation at the 9th Annual Conference on Applications of X-Ray Analysis, August 10, 11, and 12, 1960 at the Stanley Hotel, Estes Park, Colorado.

TECHNICAL OPERATING REPORT NO. 5
Project No. A-447

MECHANISM OF THE PHASE TRANSITION IN QUARTZ

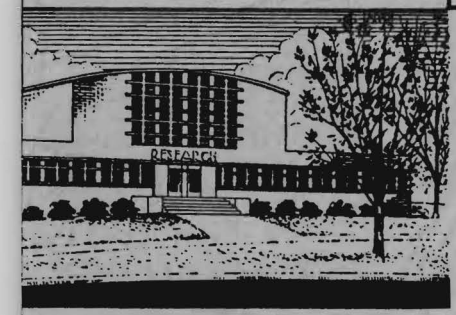
By

R. A. Young

Contract No. AF(638)-624

Air Force Office of Scientific Research
Washington 25, D. C.

July 18, 1960



Engineering Experiment Station
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MECHANISM OF THE PHASE TRANSITION IN QUARTZ

Technical Operating Report No. 5

Period Covered: 1 April 1960 through 30 June 1960

Contract No. AF(638)-624
(Project A-447)

July 18, 1960

R. A. Young
Project Director

Air Force Office of Scientific Research
Washington 25, D. C.

I. TITLE

Mechanism of the Phase Transition in Quartz.

II. OBJECTIVE AND SCOPE

The purpose of this project is to make a definitive study, by x-ray means, of the $\alpha \leftrightarrows \beta$ transition in quartz. Data will necessarily be collected at controlled temperatures near the transition temperature, 573°C. Electron density maps will be prepared corresponding to temperatures near the transition temperature. The intensity of selected reflections will be followed as a function of temperature near and, if possible, through the transition temperature. The information so obtained is expected to allow a detailed, quantitative discussion of the phase transition in terms of both the changes in the thermal vibrations and the changes in the equilibrium positions of the atoms.

III. CURRENT STATUS

A. Résumé of Work in Past Quarters

A counter-adapted Weissenberg camera is being used as the principal tool in the collection of the intensity vs. temperature data. A suitable hot air furnace has been constructed and has been described in previous reports. Specimen shaping (small spheres are used) and mounting techniques have been developed and described. Precession photographs in the ($h0\ell$) layer have been made above and below the $\alpha \leftrightarrows \beta$ transition. Some intensity vs. temperature data were collected on a few reflections, by counter means, over a temperature range which included the transition. Some interesting character in the intensity vs. temperature data for some reflections has been shown at and near the transition. Unexpected effects observed include marked increases in intensity of some reflections just below the transition and a 60° rotation of the crystallographic axes as a result of passing a crystal from the α to the β and back to the α phase.

During this quarter the principal immediate objective has remained the refinement of data already collected plus the collection of much more intensity vs. temperature data. However, as is detailed below, most of the effort has gone into (1) improvement of the data collection methods, (2) addition to the heating system capabilities and determination of its performance, and (3) the beginnings of an assessment of the magnitude and importance of certain differences among specimens.

B. Temperature Control and Measurement

1. New Furnace Mounting

In Technical Operating Report No. 4, mention was made of a new mounting of the furnace, on the counter-adapted Weissenberg, which allowed exploration of the entire zero layer and close-in upper layers without rearrangement of the furnace or thermocouples. In this arrangement the hot air stream is blown along the spindle axis directly toward the crystal and the goniometer head. An exhaust duct, slotted to allow passage of the crystal support rod, is set in between the crystal and goniometer head at an angle with the air stream. The arrangement is shown in Figure 1.

The goniometer head is protected from the hot air leaking through the slot in the duct by an aluminum foil baffle attached to the crystal support rod and by a stream of room temperature air which is played directly on the goniometer head. It was necessary to lengthen and to strengthen the crystal support rod, especially where it passes through the exhaust duct, by inserting a piece of 1/8 inch diameter ceramic tubing between the goniometer head and the quartz fiber which actually supports the crystal. With this arrangement the goniometer head does not become uncomfortably warm to the touch even though the crystal is held at 700°C.

2. Temperature Measurement

All temperature measurements are now being made with 3 mil Chromel-Alumel thermocouples. The small diameter is desirable so that the thermocouple may accurately reflect the temperature of the air stream.

That the thermocouples do follow the air stream temperature is shown by the fact that turbulent effects, in the form of thermocouple emf out-put variations as displayed on a strip-chart recorder, are observed near the edges of the hot air stream. Two thermocouples are used. The "control thermocouple", which is the sensing element for the controller (see below), is placed approximately in the center of the air stream and the leads are not allowed to touch any other part of the furnace. It was found that heat leak along the thermocouple leads, at least when 6 mil wire was used, made it impossible automatically to control the furnace temperature when the thermocouple made thermal (but not electrical) contact with the outside casing of the furnace. The measuring thermocouple is mounted on the fine positioning device, or thermocouple manipulator (also visible in Figure 1), which was completed during the quarter. This thermocouple is ordinarily brought to within a few tenths of a millimeter of the crystal during runs.

3. Temperature Control

Manual adjustment of the electric current through the furnace by means of a variac operating from a regulated supply has been used to advantage at times. A Wheelco Model 407 proportional controller, operating from the same regulated supply, has also been successfully used to maintain a nearly constant temperature.

A programmed controller was desired for several reasons. In particular, a variety of reproducible heating rates were desired. Approximation to linearity would also be convenient. Consequently, a motorized drive was designed and built which moves the control point on the Wheelco Model 407 controller at a roughly linear rate of 16°C/min when a 1 rpm Hayden motor is used. A reversing capability is built into the gear train. The drive is shown in Figure 2. It appears to work rather well, though an improvement in the quality of the gears within the controller is indicated and may be undertaken soon.

4. Performance of Heating System

Static Performance. With manual control the temperature was found to be maintained to within $\pm$ 7°C at about 650°C. With the automatic control, however, the temperature has been found to remain constant to within $\pm$ 2°C or better at about 650°C.

The temperature distribution at various temperatures and at various places in the air stream has been investigated with the help of a thermocouple manipulator. These data indicate that both at 0.5 cm and at 1.0 cm from the end of the furnace there is a region with a minimum dimension of about 2 mm over which the temperature varies by no more than $\pm$ 1.5°C at 650°C.

Dynamic Performance. With the 3 mil control thermocouple freed from thermal contact with the furnace body, the air stream temperature seems to follow the control point quite well. Figure 3 shows the indicated air stream temperature (as determined by the measuring thermocouple) as a function of the time during which the control point was being raised, with the controller drive described herein, at about 16°C/min. It is likely that most of the lack of smoothness in this curve is due to mechanical deficiencies still remaining in our drive system. Some attention may be given to correcting these deficiencies during the next quarter.

In general it may be said that the present performance of the heating system, both in terms of the temperature distribution and constancy in the static case and in terms of its dynamic behavior, is gratifying considering the relative simplicity of the equipment.

C. Dauphiné Twinning

1. The Problem

A problem has been recognized which is assumed to be due to Dauphiné twinning. While the following discussion is based on this assumption, it should be borne in mind that factors other than Dauphiné twinning may also be important.

It has been observed that the ratio of the intensity of various $(h0\ell)$ reflections to the intensity of, in each case, the corresponding $(h0\bar{\ell})$ reflection (hereafter called the $(h0\ell)$ to $(h0\bar{\ell})$ ratio) varies considerably. Variations are found even among crystals which come from the same parent single crystal; they are also found among sequential observations made with one crystal when heating through the transition has taken place between observations. This is no doubt related to the earlier observations on the 60° rotation of crystallographic axes reported in Technical Operating Report No. 3 and discussed in more detail in Technical Operating Report No. 4. For example, for the (301) reflection, the observed $(h0\ell)$ to $(h0\bar{\ell})$ ratio has varied from about 1-1/2 to 45.

Calculations based on the best positional coordinates available for quartz[1] indicate that the (301) $(h0\ell)$ to $(h0\bar{\ell})$ ratio should be about 2600. Clearly, a very serious question is raised as to the possible extent of Dauphine twinning in our crystals and its effect on our interpretation of the intensity vs. temperature data. (It is noted that a possible byproduct here may be a sensitive method of detecting the presence of small amounts of Dauphiné twinning, a circumstance which, if found in a quartz oscillator blank, should have a noticeable effect on the frequency characteristics.)

2. Other Influences on the Ratio

Primary and secondary extinction also undoubtedly play a role in the observed $(h0\ell)$ to $(h0\bar{\ell})$ ratio; the more severe the extinction the nearer unity the ratio would be. The importance of extinction can be assessed by comparing the ideal to observed ratios as a function of the structure amplitude. This has not been done systemically as yet. The effect of extinction may perhaps be minimized by working with specimens of milk quartz as they are expected to show much less extinction than does clear quartz.

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[1] R. A. Young and Ben Post, "Electron Density and Thermal Effects in α-Quartz", Paper N-3 at July, 1959 meeting of the American Crystallographic Association at Cornell University. Also Ph.D. dissertation of same name by R. A. Young, Polytechnic Institute of Brooklyn, 1959.

Other possible reasons for the variations in these ratios should not be overlooked, however. Many people who have attempted precision measurements of quartz x-ray diffraction intensities seem to have developed suspicions that effects other than extinction and twinning may be present.

3. Methods of Attack on the Problem

The elimination of Dauphiné twins by cooling through the transition in the presence of a strong electric field has been reported several times[2]. However, there is some doubt that the method was wholly successful. It is probable that considerable experimental difficulty may be encountered in providing a sufficiently parallel electric field of proper strength and orientation at the crystal while it is being examined with x-rays as it goes through the transition. Application of a 900 V potential difference between the control thermocouple and the exhaust duct produced no measurable effect. It is possible that properly controlled thermal gradients could eliminate Dauphiné twinning; this approach has not been investigated at all so far.

At present, efforts are being directed toward determining the nature of the influence of the supposed Dauphiné twinning on the intensity vs. temperature data of several reflections near the transition temperature. It is hoped that either the influence will be found to be negligible (which seems unlikely) or that correlations between the magnitude of the influence and the observed ratios can be made which in turn will make possible the correction of the data for the twinning.

Another possible approach, which seems unattractive if one of the above approaches will work, is to use the (h0ℓ) to (h0$\bar{\ell}$) ratios at room temperature to determine as well as possible the amount of Dauphiné twinning present and then to compute corrections to the intensity vs. temperature data on that basis.

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[2] See, for example, E. V. Tsinzerling, "Artificial Stabilization of the Structure of Quartz", Doklady Akad. Nauk. SSSR 95, 529-30 (1954); Abstract in Chemical Abstracts 48: 13558g.

D. Data Collection

1. Collection Schemes

Because so very many data are required before serious analysis can begin, attention must be given to the time involved in various possible alternate methods of collecting the data. The intention is to concentrate first on the (h0ℓ) data of one crystal determined to be typical.

It was mentioned in the last report that the (h0ℓ) data collection would begin with measurements at room temperature, 550°C, and 650°C. This plan has been abandoned in favor of continuous intensity vs. temperature (or intensity vs. time) data now that a reproducible and approximately linear heating rate is available.

The current plan is to collect the data from room temperature to about 500°C with a heating rate of 64°C/min. and to collect the data from about 500°C to 600°C with a heating rate of 16°C/min. At a later time, the temperature range in the intermediate neighborhood of the transition (573°C) will be examined with slower heating rates. (This may require further modification of the gear train which now drives the controller set-point.) It is estimated that the collection of all of the (h0ℓ) data of one crystal will require about 10 working days per crystal per temperature range covered with no time allowed for repairs, adjustments, changes, etc. The probable actual time then will be 2 to 3 times as long or up to 50 working days per crystal for just the first run-through on peak intensity vs. temperature from room temperature to 600°C for the (h0ℓ) reflections. In addition, the relationship of the integrated intensities to the peak intensities must be determined as a function of temperature and of Bragg angle and the transition region of at least most reflections must be examined still more closely. Also required will be good relative intensity data on all observable (hkℓ) reflections at room temperature. Intensity vs. temperature data on at least many of the (hkℓ) reflections would be desired. Before a "typical" set of data can be gathered, however, the Dauphiné twinning and the extinction problems must be circumvented. Thus it appears that a great deal of experimental work and data collection lies ahead before analyses of the data for crystal structural information should be started.

2. Data Collected

Data collected during the quarter include intensity vs. temperature data for a few reflections from room temperature to 600°C, further demonstration of the reality of the sharp increases in intensity in certain reflections just below the transition, and measurements of a number of $(h0\ell)$ to $(h0\bar{\ell})$ ratios for several crystals, including a synthetic quartz crystal previously examined by the author[1].

E. Specimen Mounting

The requirements on the mounting of the crystals are more stringent now than ever before. The crystal is mounted with Sauereisen cement on a short quartz fiber which in turn is mounted on a 1/8 inch diameter ceramic tube. The tube is mounted on a brass plug which serves as an insert for the goniometer head. The total crystal-to-brass-plug distance is held to about $\pm$ 1 mm so that it may be near to the maximum usable length. The crystal is mounted so that the desired rotation axis lies within less than 5° of the mounting fiber axis in order that the ceramic tube shall not collide with the sides of the exhaust duct when the crystal is in position for data collection. Crystals are sometimes mounted 3 or 4 times with collodion and Formvar before the desired orientation is obtained and the final mounting is made with Sauereisen cement. Total effort required for complete mounting of one crystal is about 1 to 1-1/2 man-days.

F. Computing

Mention was made in the last report of negotiations in progress with the OSR Contract Office and the National Bureau of Standards to make use of the IBM 704 machine and computer group at NBS. With the particular help of Mr. Swerdlow of OSR, the necessary approvals have now been secured. Use will probably not be made of this facility until the seriousness of the Dauphiné twinning problem has been better assessed and a number of "typical" intensity vs. temperature data have been collected.

IV. PLANS FOR FUTURE WORK

The principal effort will continue to be spent on means for assessing the seriousness of and for circumventing the Dauphiné twinning problem. When this has been accomplished a variety of crystals will be spot-checked (the checks now in progress on $(h0\ell)$ to $(h0\bar{\ell})$ ratios are a start on this) for the purpose of finding a "typical" crystal on which the whole set of $(h0\ell)$ intensity vs. temperature data will be collected according to plans discussed in the last section.

Some of the problems that have not yet been dealt with definitively are those of extinction and of the possibility of thermal gradients in the specimen. These will be dealt with when necessary.

Since the quartz crystals expand on heating, it is necessary continuously to readjust the spindle setting (on the counter-adapted Weissenberg) slightly. This is presently accomplished by a trial and error method. Some attention will be given to the problem of doing this more systemically or perhaps automatically.

V. PERSONNEL

Mr. William A. Stephens has joined the laboratory for the summer and will spend the major portion of his time on this project. Mr. Stephens has just graduated from high school where he maintained a straight A average for the entire high school period. He will enter Georgia Tech as a freshman in Physics in September, 1960. His association with us appears to be of mutual benefit and we hope that he will be able to continue to spend a few hours a week with us throughout the school year.

VI. BUDGETING MATTERS

Approximately $28,000 are left in the contract as of 30 June 1960. A no-cost extension, mentioned several times before, is still being planned. The request for this extension is being delayed so that a better estimate, based on a better assessment of the project personnel situation, can be made.

Respectfully submitted,

R. A. Young
Project Director

Approved:

Vernon Crawford, Head
Physics Branch, Physical Sciences Division

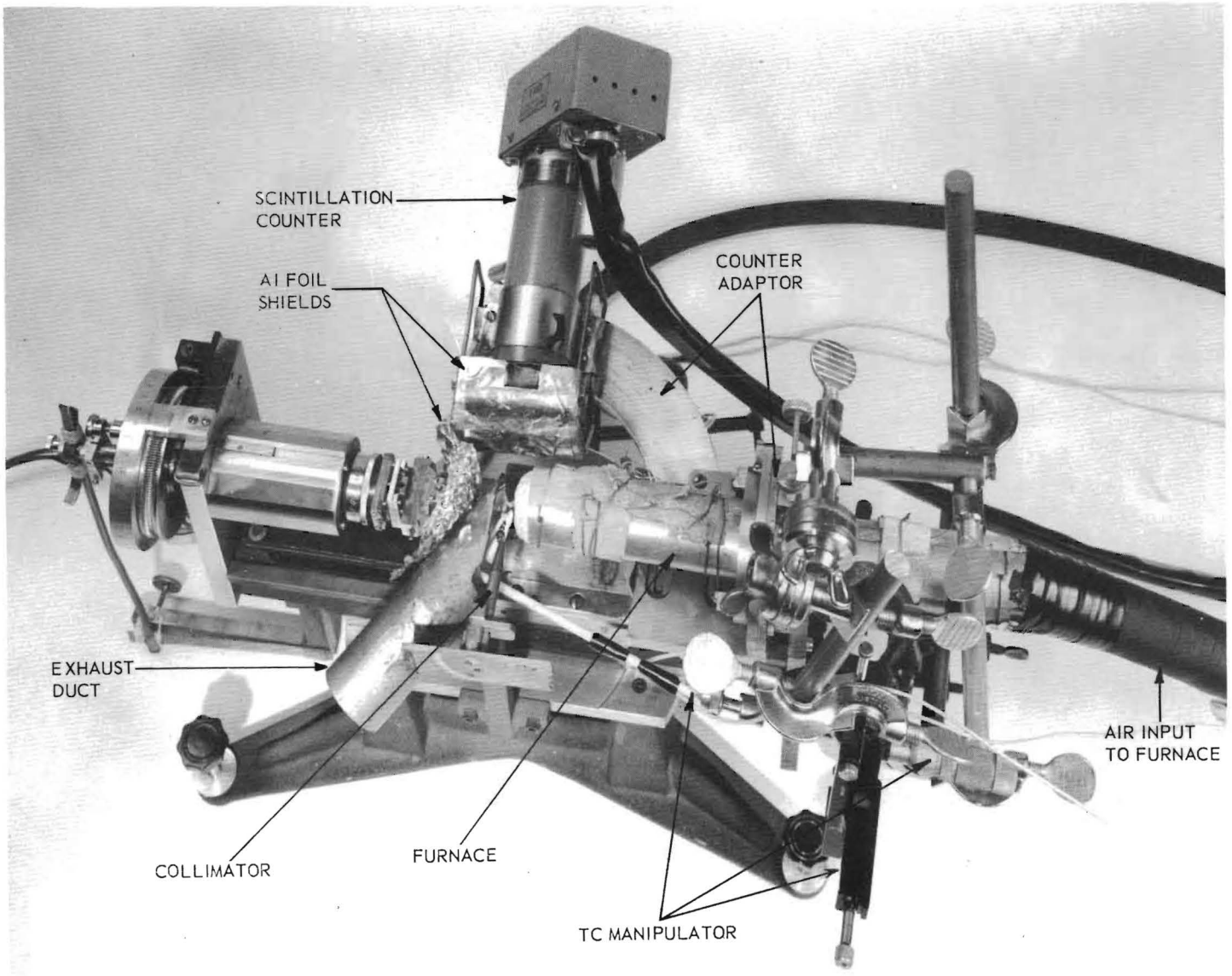


Figure 1. Furnace on Counter - Adapted Weissenberg.

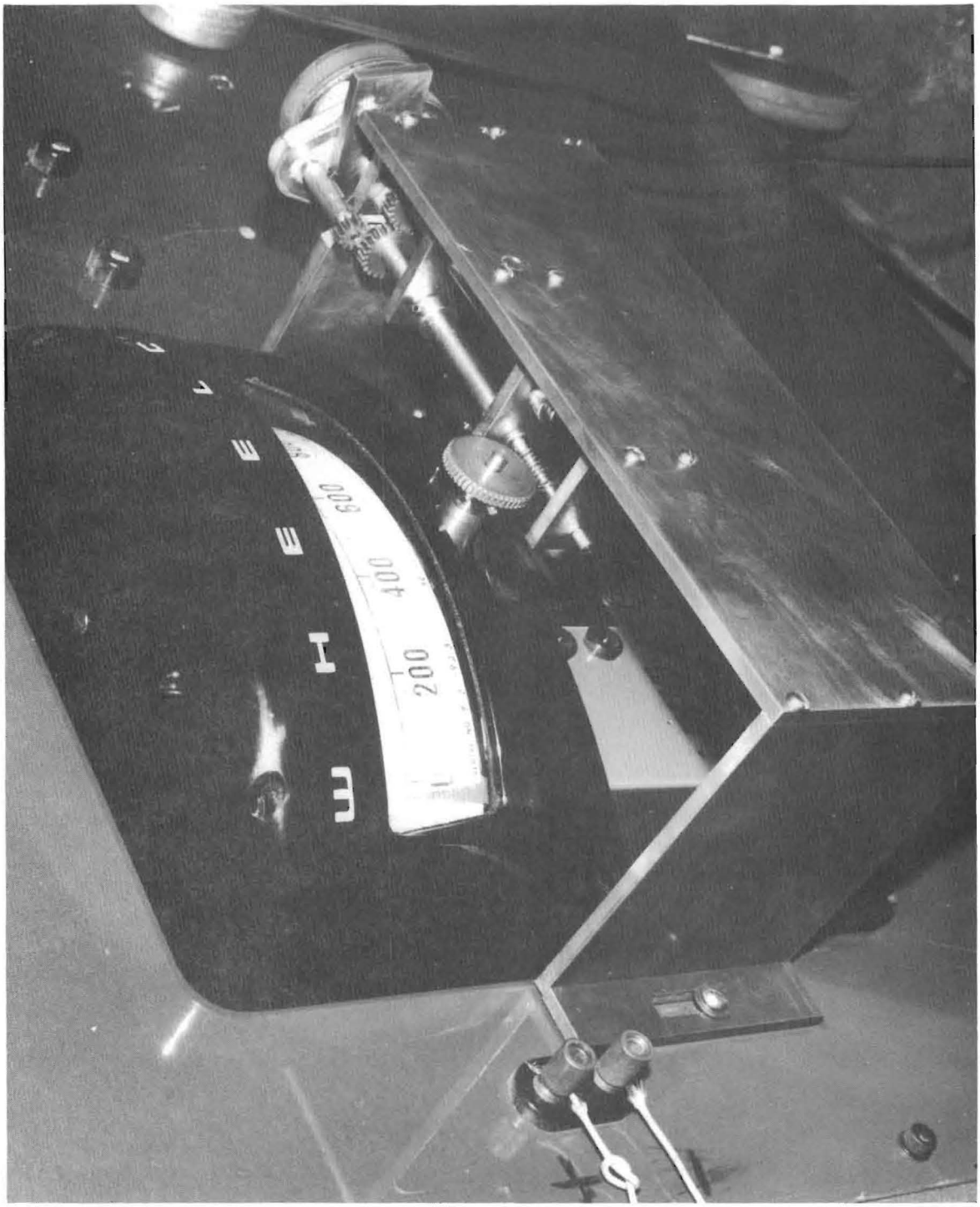


Figure 2. Control Point Drive.

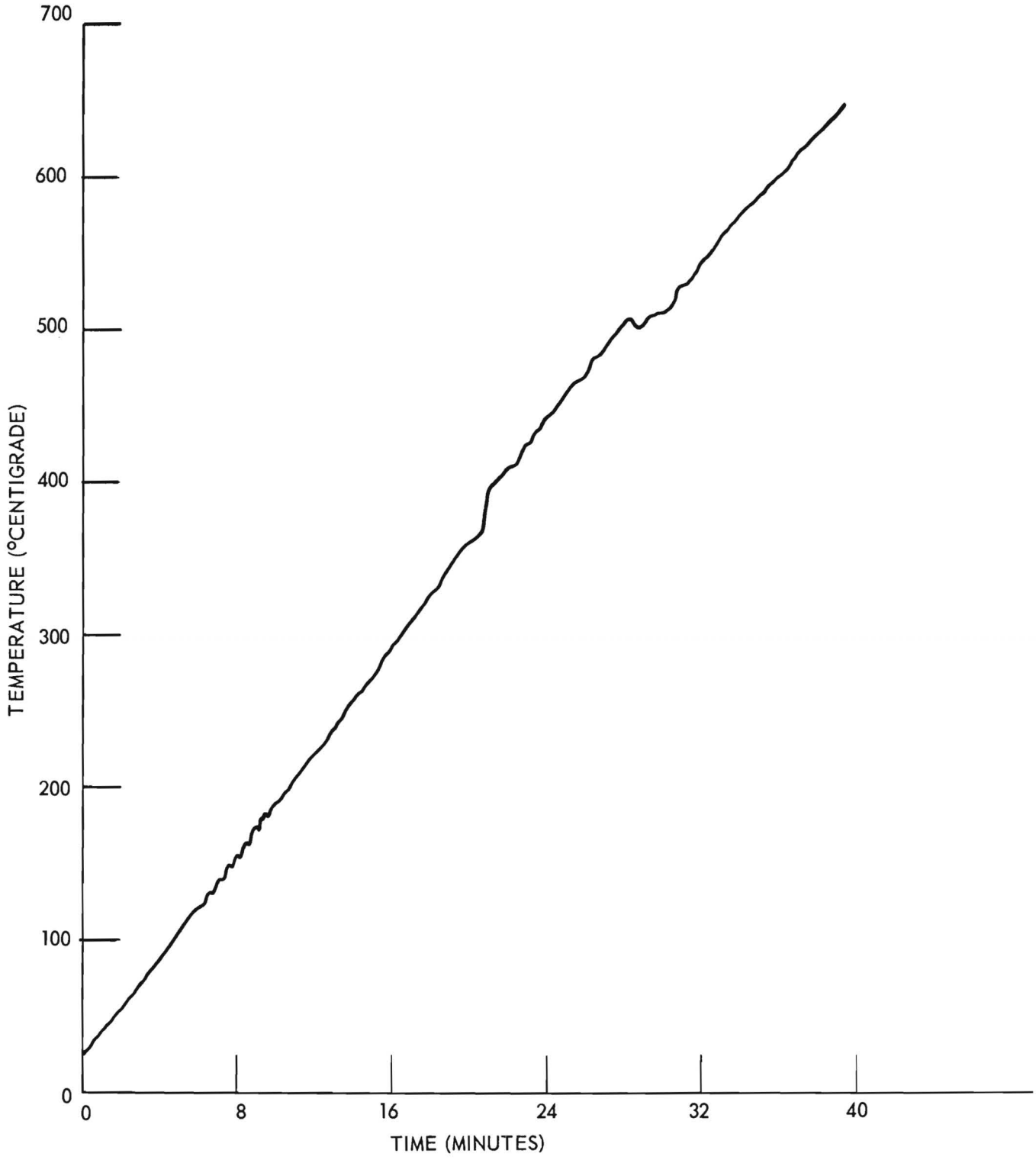


Figure 3. Dynamic Performance of Heating System.

TECHNICAL OPERATING REPORT NO. 6
Project No. A-447

MECHANISM OF THE PHASE TRANSITION IN QUARTZ

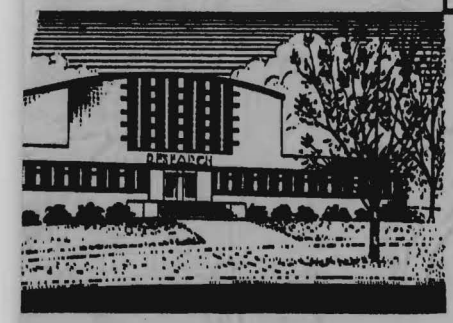
By

R. A. Young

Contract No. AF(638)-624

Air Force Office of Scientific Research
Washington 25, D. C.

October 14, 1960



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MECHANISM OF THE PHASE TRANSITION IN QUARTZ

Technical Operating Report No. 6

Period Covered: 1 July 1960 through 30 September 1960

Contract No. AF(638)-624
(Project A-447)

October 14, 1960

R. A. Young
Project Director

Air Force Office of Scientific Research
Washington 25, D. C.

I. TITLE

Mechanism of the Phase Transition in Quartz.

II. OBJECTIVE AND SCOPE

The purpose of this project is to make a definitive study, by x-ray means, of the $\alpha \overleftrightarrow{\rightarrow} \beta$ transition in quartz. Data will necessarily be collected at controlled temperatures near the transition temperature, 573° C. Electron density maps will be prepared corresponding to temperatures near the transition temperature. The intensity of selected reflections will be followed as a function of temperature near and, if possible, through the transition temperature. The information so obtained is expected to allow a detailed, quantitative discussion of the phase transition in terms of both the changes in the thermal vibrations and the changes in the equilibrium positions of the atoms.

III. CURRENT STATUS

General Summary

The principal effort during the quarter has been directed to the problem of Dauphiné twinning and extinction. Both are very serious problems. They are aggravated by a lack of reproducibility of the magnitudes of the effects even among specimens taken from the same parent crystal. In the case of Dauphiné twinning the effect is not reproducible from time to time with the same specimen if it has been heated (not necessarily through the transition) between observations. A plan of attack has been devised which may circumvent the Dauphiné twinning problem in so far as a determination of the $\alpha \overleftrightarrow{\rightarrow} \beta$ transition mechanism is concerned. Possible methods for correcting for extinction are being considered.

Some minor changes were made in the equipment.

A paper on the "Counter Adaptor and Furnace for a Weissenberg Camera" is being prepared as a technical note.

Dauphiné Twinning

A series of experiments were carried out to determine something of the reproducibility and conditions for change in the degree of Dauphiné twinning in quartz. Changes or differences in $ho\ell/ho\bar{\ell}$ ratios* were used as principal indicators of changes or differences in the degree of Dauphiné twinning. Some (00ℓ) reflections, which are not affected by Dauphiné twinning, were also observed in order to make it possible to distinguish between changes in twinning and changes in extinction.

Among several spherically ground specimens taken from the same parent crystal (#2--Clear Georgia quartz) the initial room temperature $301/30\bar{1}$ ratios (which are particularly sensitive to Dauphiné twinning) varied from 1.2 to 250 (theoretical ratio in the absence of twinning and extinction is about 2600). While some of this variation is due to extinction differences, most is due to differences in Dauphiné twinning.

The effect of heating through the transition of, at least the effect of the subsequent cooling, is generally to change the degree of twinning toward an equal distribution of the two kinds of twins. It is not necessary to raise the temperature to the transition temperature in order that subsequent cooling can produce changes in twinning. The behavior of the $301/30\bar{1}$

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* i.e., the ratio of the intensity of an $(ho\ell)$ reflection to that of the corresponding $(ho\bar{\ell})$ reflection

ratio of a particular specimen (2E) serves to illustrate these points. The initial room temperature ratio was 60. When the crystal was heated to 500° C no change with time could be detected in the 301/30$\bar{1}$ ratio at 500° C but when the crystal was cooled to room temperature the ratio had dropped to 45. After the crystal was then heated to 650° C and cooled the ratio had dropped to 1.1. Throughout this procedure the measured (00ℓ) relative intensities agreed within $\pm$2%, thus changes in extinction are assumed to be absent.

Since the general trend with heating is toward an equal amount of each kind of twin, then in this sense the specimens are made more nearly alike by heating. Not all crystals behave the same even in this respect, however: one crystal developed an 301/30$\bar{1}$ ratio of 8 which could be changed to 1/8 and back to 8 by heating but which did not approach any nearer to unity. Thus the crystal behaved as though it were divided into 2 definite regions, of unequal size, one of which was required to be the Dauphiné twin of the other.

The literature[1,2] cites three ways of producing twins in an initially untwinned crystal: (1) by cooling through the transition temperature, (2) by cooling, presumably fairly rapidly, from temperatures which are below the transition temperature and may be as low as 200° C, and (3) by mechanical deformation. It is possible that our grinding technique is producing twinning by mechanical deformation. Etching the ground surfaces of some of the crystals in 50% HF acid for 30 minutes produced a visible change in the otherwise frosted appearance of the surface but did not affect, for example, the 301/30$\bar{1}$ ratio appreciably. Further, the variation in intensity ratios seems too large to be only a surface effect.

Since the $ho\ell/\bar{h}o\bar{\ell}$ ratios (nearly unity, as the specimen are approximately spherical) are consistently unchanged by treatment that changes the $ho\ell/ho\bar{\ell}$ ratios, it appears that the twinning must take place fairly homogeneously throughout the specimen, perhaps mosaic block by mosaic block.* This is suggested in spite of the fact that both the literature and our microscopic observations of a quartz oscillator blank, twinned from having been dropped while hot onto a wet towel, indicate that Dauphiné twins occur habitually as one kind only over relatively large regions. There is no indication in those cases of an apparently nearly homogeneous distribution of twins such as we deduce from our observations of diffracted x-ray intensities.

This brings up the point of whether some oscillator blanks, which are declared twin-free on the basis of etch tests but behave poorly in frequency tests (particularly when operated in the higher overtone modes), may not in fact contain many twins of microscopic, perhaps of mosaic block, size. Some tests of this point are being planned in connection with (and at the expense of) another project.

The literature reports attempt at detwinning which met with varying success. Tsinzerling[6], for example, recommends slowly cooling the crystal through the transition while causing it to oscillate (piezoelectrically) at its resonant frequency. U. S. Patent 2,767,067 describes a device for the purpose. However, it is difficult to see how this technique might be

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* If large sections of the crystal were involved with one kind of twin only, it would be expected that, as $(ho\ell)$ and $(\bar{h}o\bar{\ell})$ reflections were observed, first one and then another such section would, because of absorption, be in the more favorable diffracting position. Hence observed $(ho\ell)$ and $(\bar{h}o\bar{\ell})$ intensities, both of which arise in fact from a superposition of the $(ho\ell)$ intensity of one twin with the $(ho\bar{\ell})$ intensity of the other, would be expected to differ.

conveniently applied to our small spherical specimens. We have considered using the $ho\ell/ho\bar{\ell}$ ratios obtained from a piece of oscillator-blank quartz, shown by etch tests to be twin-free, to tell as what these ratios "ought" to be. One might then hope to correct the observations of intensity as a function of temperature for a known amount of Dauphiné twinning; as was suggested in T. O. Report No. 5. However, several things are against this: (1) Such "standard" ratios would still have to be corrected for extinction. (2) The etch test does not guarantee the absence of microscopic twins. (3) Since the degree of twinning has been shown to change below the transition temperature, one would be in the position of trying to correct for a factor that was not only specimen but also temperature dependent to an unknown degree.

Tests were made on a number of crystals from various sources to see if the relative intensities in the β-phase depended on the Dauphiné twinning history in the α-phase. As expected, no such dependence was found. Thus, it was decided to avoid the Dauphiné twinning problem, at least for a time, by working first in the β-phase.

It seems it should be possible to determine the structure in the β-phase just above the transition temperature with considerable precision. This structure can then serve as a starting point for a study of the actual mechanism of the transition (including a precise determination of the structures just below the transition) based on the changes of intensity of those reflections which are not affected by Dauphiné twinning, namely (hh0) and (00ℓ) reflections. It is possible that following the change in value of the sum

$\left(|F_{ho\ell}|^2 + |F_{ho\bar{\ell}}|^2\right)$, as the specimen is taken through the transition, will also be of value. Determining a structure from such information would seem on first thought, at least, to be equivalent to replacing the actual unit cell by one made up from the superposition of the unit cells corresponding to each of the two twin orientations.

Clearly an approach based on using the β-structure as a reference point promises to make it possible completely to avoid the Dauphiné twinning problem while fulfilling the goal of the present project: determination of the mechanism of the $\alpha \leftrightarrows \beta$ transition. The Dauphiné twinning problem is of interest in itself, however. Perhaps we will be able to return to it at some future time.

Extinction and other variants

Extinction appears to remain as the biggest problem in the experimental determination of structure amplitudes. The relative intensities of several reflections in the β-phase (which are not affected by Dauphiné twinning) were checked for 15 specimens from 6 parent crystals comprising Bell Labs synthetic, Georgia clear, Georgia milk, Brazilian and two samples (rose and clear) from Dr. Tuttle's (Penn State) collection. Considerable variation among specimens was found, even among specimens taken from the same parent. For example, the (101)/(003) intensity ratio varied from 35 to 115 among 3 "#2--Georgia, clear" specimens and from 34 to 56 for 2 specimens taken from parent crystal #7, which is a particularly well-behaved sample from Dr. Tuttle's collection (i.e., he found no hysteresis in the transition, he found the transition to take place at the "right" temperature, and the crystal appears clear).

Thus, it appears that the original parent crystals are far from homogeneous with respect to relative intensity measurements. Inhomogenities in nearly perfect quartz crystals were demonstrated by Bond and Andrus[7] with an x-ray diffraction topographic technique. They found both slight misorientations between adjacent regions (generally of mm size) and very small differences in d-values from place to place. It is not surprising that the severity of extinction should also vary from place to place in the parent crystal. While the observed variations in relative intensities could, in principle, be due at least in part to causes other than extinction, e.g., impurities, real differences in electron density distributions, real differences in coordinate and thermal parameters, it seems probable that most if not all of the variations are due to extinction. The observation that the variations are greatest for the strongest reflections is in agreement with such an assumption.

It would seem to be pointless, if avoidable, to collect β-phase relative intensity data for structure determination on specimens not typical of the parent crystal as a whole. The Georgia milk-quartz seems most promising in the respect, as the relative intensity variations among specimens are less for this material than for the others so far studied. Further assessment of this variation is being made.

One point in using crystals typical of the parent is to allow meaningful comparisons of single crystal data with powder data -- the powder to be obtained by grinding up a portion of the parent crystal. Such comparison might form the basis for making corrections for extinction.

There is no guarantee, however, that the extinction will be isotropic. It is generally recognized that any wholly valid correction for extinction must be made reflection by reflection. The influence of extinction may be detected in several ways, among which are (1) the dependence of diffracted intensity on the direction of polarization of a plane-polarized incident beam, (2) the wave-length dependence of relative intensities, and (3) the effect of extinction on the integral breadth of rocking curves. The method involving rotation of the plane of polarization, credited to S. Chandrasekhar[8] seems especially interesting, particularly since K. S. Chandrasekharan has just published a paper[9] which gives a more comprehensive discussion of the basis of the method, extends it somewhat, and reports on experimental investigations of the method.

Equipment

Only minor changes were made in the equipment during the quarter. When the furnace was accidentally burned out advantage was taken of the opportunity to rebuild it along improved lines which consist mainly of an improvement in the side wall insulation properties with no increase in external diameter. Also it has been found possible to do without the exhaust duct, shown in Figure 1 of T. O. Report No. 5, for most of the high temperature work. The absence of the duct makes it possible to mount the specimens more simply and greatly to reduce the danger of their being accidentally knocked off their fiber mountings. A number of other small changes were made.

IV. FUTURE WORK

Experimental work during the next quarter will be directed toward collecting reliable relative intensity data in the β-phase from a crystal typical of its parent. This involves the selection of the crystal (probably

Georgia milk quartz), collection of maximum peak intensities, and collection of sufficient additional data to convert peak intensities to integrated intensities. (hoℓ) zone data will be concentrated on at first. The weaker reflections will receive particular attention because of their relative freedom from extinction.

Possible methods for correcting for extinction will be examined further.

In subsequent quarters, after the β-phase structure has been successfully determined at a few degrees above the $\alpha \rightleftarrows \beta$ transition temperature, attention will be directed toward using the changes of intensity of the (hko) and (00ℓ) reflection to determine the changes that take place in both coordinate and thermal parameters as the quartz specimen is cooled through the transition. If successful, this approach will achieve the goal of the project.

V. OTHER ACTIVITIES

A paper, based in part on project work, was presented at the 9th Annual Denver Conference on Applications of X-ray analysis which was held in Denver, Colorado on 10-12 August, 1960. The full text will appear in the "Proceedings" of the conference and it is also being submitted to OSR as a Technical Note. The title of the paper is "Counter Adaptor and Furnace for Weissenberg Camera." Travel costs were borne in part by this project.

A visit was received from Major Ronald Sellers of the Solid State Sciences section, on 13 July, 1960. We particularly welcomed this opportunity to show our facilities and to discuss at some length our progress, problems, and aspirations.

VI. PERSONNEL

Mr. Donald Battson, Research Assistant, ended his association with our laboratory as of 30 September, 1960. On 3 October, 1960, Mr. N. Kelley Hearn will assume the duties previously assigned to Mr. Battson and will spend 2/3 time on this project. Mr. Hearn has a B.S. in Physics from Kansas State Teacher's College (Emporia) and has 3 years experience as a physicist in industry. About 1/3 of his experience is in x-ray and electron diffraction. He will do part time graduate study in Physics. All indications are that he will be a great help to the project.

Mr. W. A. Stephens, who was mentioned in the last report, has now entered Georgia Tech as a freshman in Physics. As a result he now spends only about 10 hours per week on project work. His performance of project work during the quarter has been remarkably good. He exercises a degree of intellectual acumen, ingenuity, and logical discipline both in performing and writing up his work which is most unusual for an undergraduate.

VII. BUDGETARY AND ADMINISTRATIVE MATTERS

Approximately $20,680 was left in the contract budget as of 30 September, 1960.

It has been mentioned in several previous reports that a no-cost extension of the performance period was to be requested. The personnel situation now seems to have been cleared up and a request for a six-month extension has been made.

Respectfully submitted,

R. A. Young
Project Director

Approved:

Vernon Crawford, Head
Physics Branch, Physical Sciences Division

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TECHNICAL OPERATING REPORT NO. 7
Project No. A-447

MECHANISM OF THE PHASE TRANSITION IN QUARTZ

By

R. A. Young

Contract No. AF(638)-624

Air Force Office of Scientific Research
Washington 25, D. C.

March 1, 1961

Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

MECHANISM OF THE PHASE TRANSITION IN QUARTZ

Technical Operating Report No. 7

Period Covered: 1 October through 31 December 1960

Contract No. AF(638)-624
(Project A-447)

March 1, 1961

R. A. Young
Project Director

Air Force Office of Scientific Research
Washington 25, D. C.

October 1 through December 31, 1960

I. TITLE

Mechanism of the Phase Transition in Quartz

II. OBJECTIVE AND SCOPE

The central objective of this study is the determination of the mechanism of the phase transition in quartz. An x-ray diffraction method is to be used; the mechanism is to be described in terms of the changes that occur in the equilibrium positions and thermal vibrations (thermal ellipsoids) of the atoms as the crystal undergoes the transition at about 573° C. The study is to entail first refining either the α- or β-structure at a temperature near the transition temperature used. The temperature dependences of selected Bragg intensities, measured individually as continuous functions of temperature, will then be used to establish the atomic positional and vibrational changes that take place as the crystal temperature is varied to and through the transition temperature. Precision measures of intensities and changes in intensities (and of structure amplitudes) are emphasized. Nearly all quantitative data will be collected with the use of a counter-adapted Weissenberg camera provided with a flexible, controllable ($\pm$ 3° C or better) hot air furnace. Various features of the technique, measurements made, sources of error considered, and handling of the data reflect the effort to obtain precision.

Refinements and other analysis procedures will include both a least squares approach (using individual, anisotropic temperature factors) and Fourier synthesis (electron density and Patterson maps) methods.

A variety of specimens is to be included in the study in order that the results may be applicable to "quartz" rather than only to a particular sample.

As time permits, the studies of changes in coordinate and thermal parameters will be extended to cover the 100° C or so region just below the transition in order that correlations may be attempted with the marked changes in various physical properties which occur in this region.

III. CURRENT STATUS

A. General Summary

At the end of the last quarter it was pointed out that efforts would be directed toward refining the β-structure (and using it as a starting configuration in the transition studies) in order to avoid certain problems with Dauphiné twinning in the α-form.

Considerable progress was made during the present quarter in gathering the necessary β-phase x-ray data, in further minor improvements of the temperature control and measurement apparatus and procedures, and in the measurement, control, and understanding of the background intensity. Progress in each of these three areas is discussed separately. The principal pieces of x-ray apparatus being used are still the counter-adapted Weissenberg camera (see Technical Note No. 1 for description) and a precession camera. The specimens on both "cameras" are heated by a hot air stream.

B. Temperature Measurement and Control

1. Equipment modification

a. Furnace

Excessive thermal lag developed in the furnace, which made it difficult or impossible to utilize automatic control with present equipment (described in previous quarterly reports and in Technical Note No. 1). It was found that the porous firebrick plug at the exit end had become clogged and it was suspected that the heat capacity of the alumina bubbles in which the heating coils were packed might be excessive. All of the alumina bubbles were removed from the main body of the furnace (except those which incidentally stuck in the wire heating coils). The firebrick plug was replaced by a "plug" consisting of about 1 cm of alumina bubbles held in place by brass screens at either end. These changes produced excellent results. On automatic control the furnace now stabilizes at 500° C in about 3 minutes from a cold start (room temperature) and, of course, shows correspondingly rapid recovery after any demanded temperature change is made. The dynamic characteristics are also much improved in regard to following a demanded constant rate of change of temperature.

b. Protection of apparatus from heat

Further minor changes have been made in the methods of protecting the various parts of the apparatus from the hot air blast which is used to heat the specimens.

(1) Counter-adapted Weissenberg camera

It was mentioned in the last report that the hot-air exhaust duct, described in Technical Note No. 1 for mounting the furnace co-axially with the Weissenberg spindle axis, had been abandoned. A simple aluminum foil shield was being used then to protect the goniometer head. A wholly satisfactory arrangement has now been made. It is shown in exploded view in Figure 1 and in place in Figure 2.

The spherical-section cap is made of aluminum covered by asbestos paper and is free to rotate on the shaft of the brass fiber-mounting plug. The notch in the cap allows access to the arc adjustments on the goniometer head. A room temperature air stream played on the lower back side of the cap keeps the goniometer head always cool enough to touch with one's fingers. This air stream yields the unexpected bonus of carrying off with it the bulk of the main hot air stream. It thus protects other parts of the apparatus (e.g. the base of the Weissenberg) as well. The flow pattern is apparently somewhat as indicated in Figure 3.

The result is that the region between the spindle and the base of the Weissenberg remains quite cool, practically all of the hot air goes off in a rather well defined stream directed well away from all parts of the apparatus.

(2) Precession camera

As has been pointed out in previous reports, the same hot air furnace may be used both on the counter-adapted Weissenberg camera and on the precession camera to produce and maintain specimen temperatures up to about 700° C. An attractively simple and positive method was developed for protecting the layer screen and film from the hot air stream. Because of the placement of camera parts the furnace cannot be mounted (stationary)

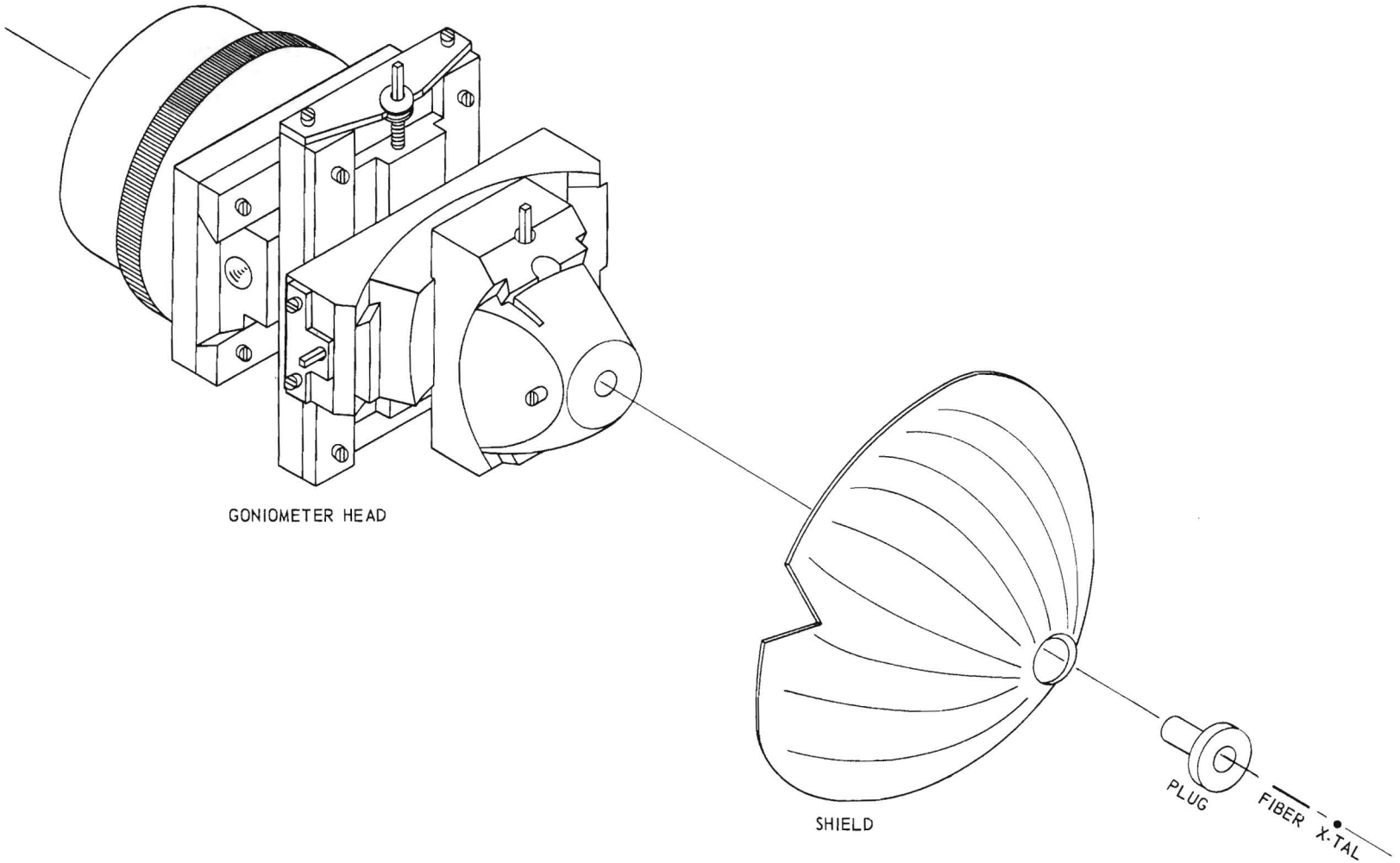
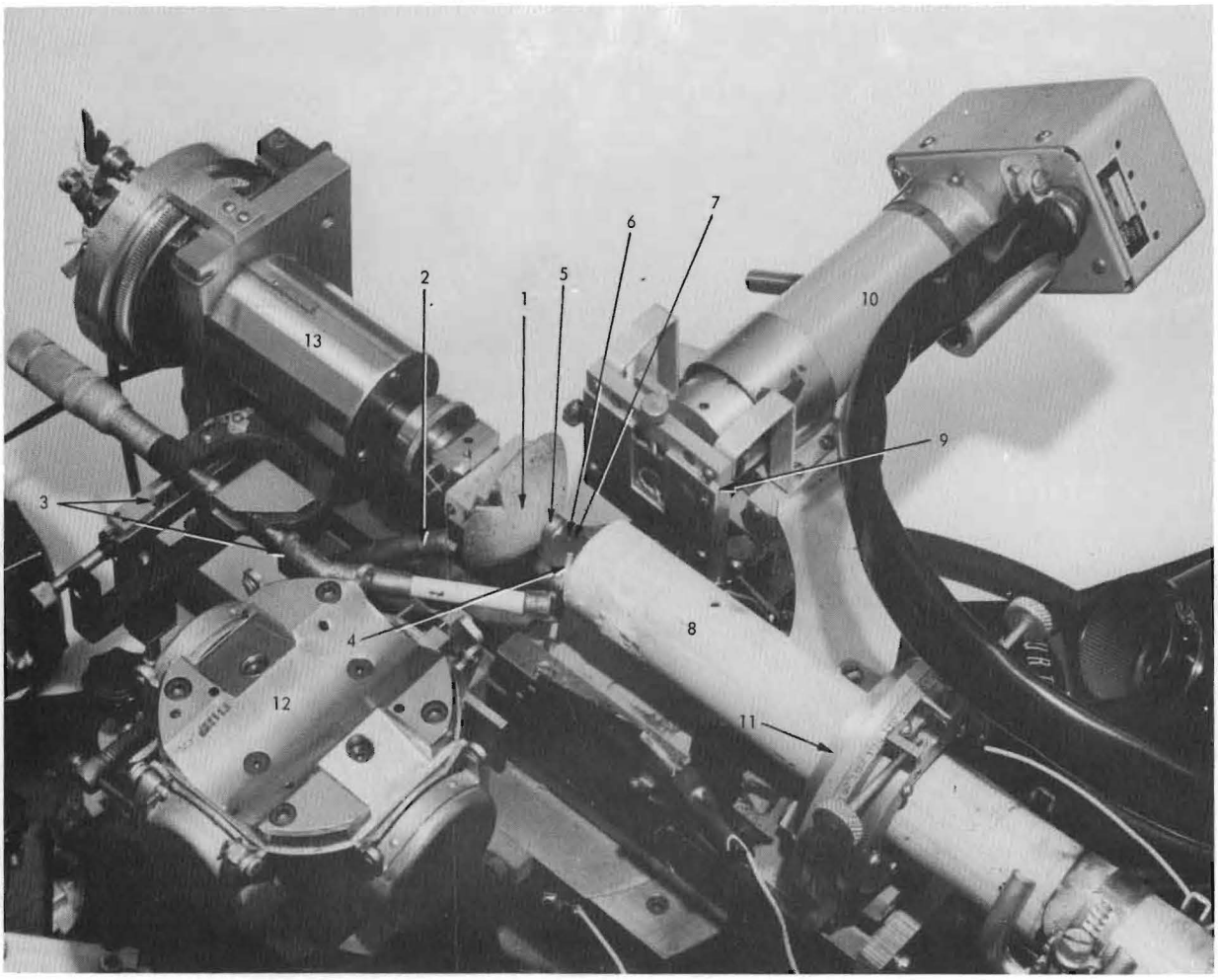


Figure 1. Exploded View of Goniometer Head and Heat Shield.



1. Goniometer Heat Shield
2. Room Temperature Air Stream
3. Thermocouple Manipulator
4. Thermocouple Support
5. Brass Mounting Plug
6. Fuzed Quartz Mounting Fiber
7. Quartz Crystal
8. Furnace
9. Combination Counter Heat Shield and Front Aperture Support
10. Scintillation Counter
11. Υ Scale of Counter Adaptor
12. X-ray Tube Head
13. Weissenberg Spindle Housing

Figure 2. Counter-Adaptor, Furnace, and Accessories in Place on Weissenberg Camera Base.

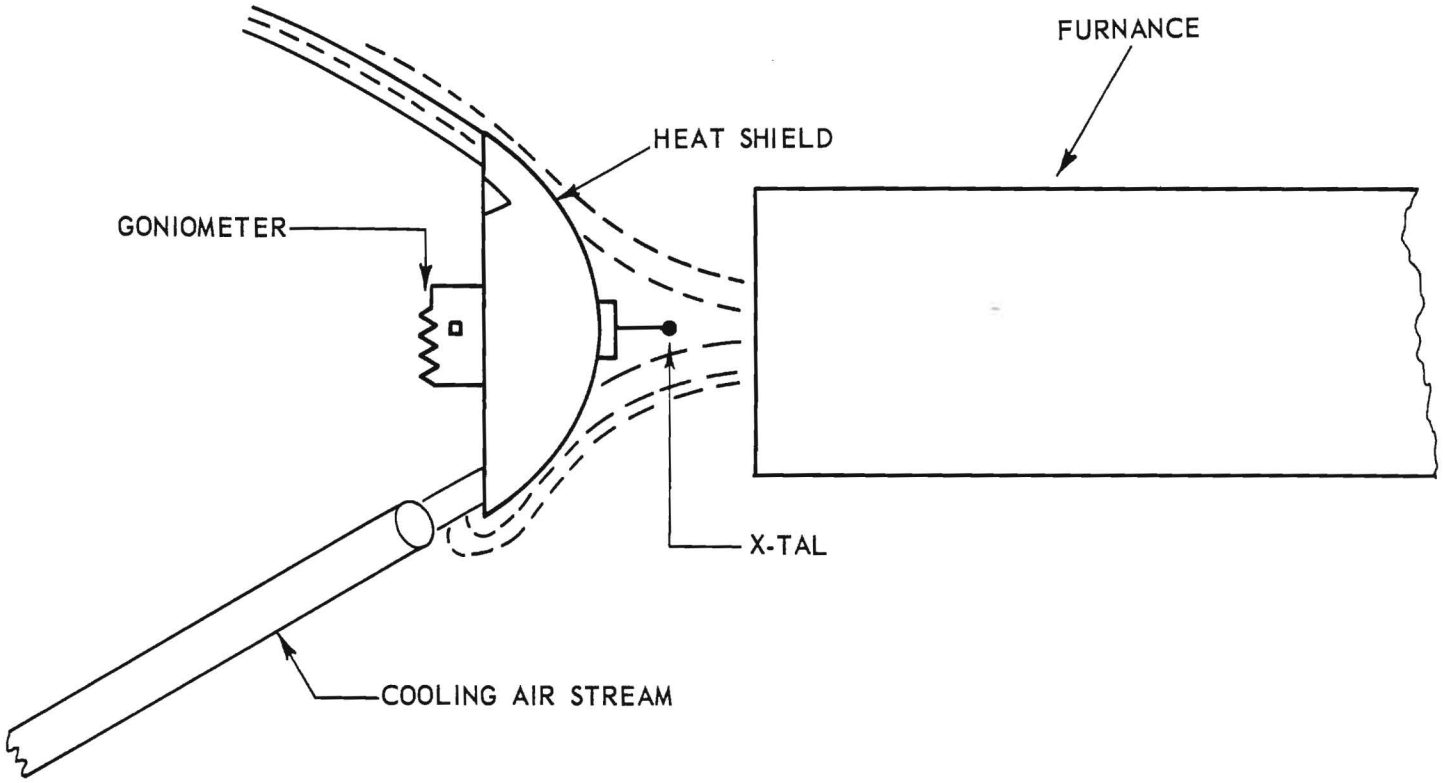


Figure 3. Air-Flow Diagram.

with the hot air stream perpendicular to the x-ray beam axis without severely restricting the maximum precession angle; it is mounted to blow down and slightly toward the film. A protective curtain of room temperature air is provided on the front surface of the layer screen from a short length of copper tubing which is sealed at the end, has a number of small holes along its side, and is mounted on and parallel with the top edge of the layer screen holder. The layer screen is covered with one layer of Al foil to help smooth the flow pattern and to provide some radiation shielding between the film and the hot region around the specimen. The protection so afforded appears to be excellent; no carefully shaped or placed exhaust duct is needed; the main portion of the hot air stream may be allowed to play on a sheet of asbestos paper placed over the base of the yoke out of the way of all diffracted x-ray beams. The arrangement is shown in Figure 4 without the asbestos paper. A full 30° precession angle is obtained "at temperature," which may be any temperature from room temperature to 700° C.

2. Significance of indicated temperature

The following discussion is in the context of operations with the counter-adapted Weissenberg.

The temperature stability at 600° C is now about $\pm 2^{\circ}$ C.

The temperature distribution over a 1 mm^2 cross-section area including the crystal (which is usually from 0.2 to 0.4 mm in diameter) appears to be constant within $\pm 1^{\circ}$ C at about 600° C.

Calibration of the indicated temperature, as measured with a small thermocouple in the air space a few tenths of a mm from the specimen*, against the actual specimen temperature is accomplished to within 1 or 2° C in the following manner. A particular specimen, #7-A, has been prepared from a sample supplied by Dr. Tuttle of Pennsylvania State College. During

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*The manipulator which gives screw controlled (to about 0.01 mm) motion in 3 dimensions and the section of ceramic tube which supports the 3 mil thermocouple can be seen in Figure 2. On the original photograph the 3 mil thermocouple wires can also be seen.

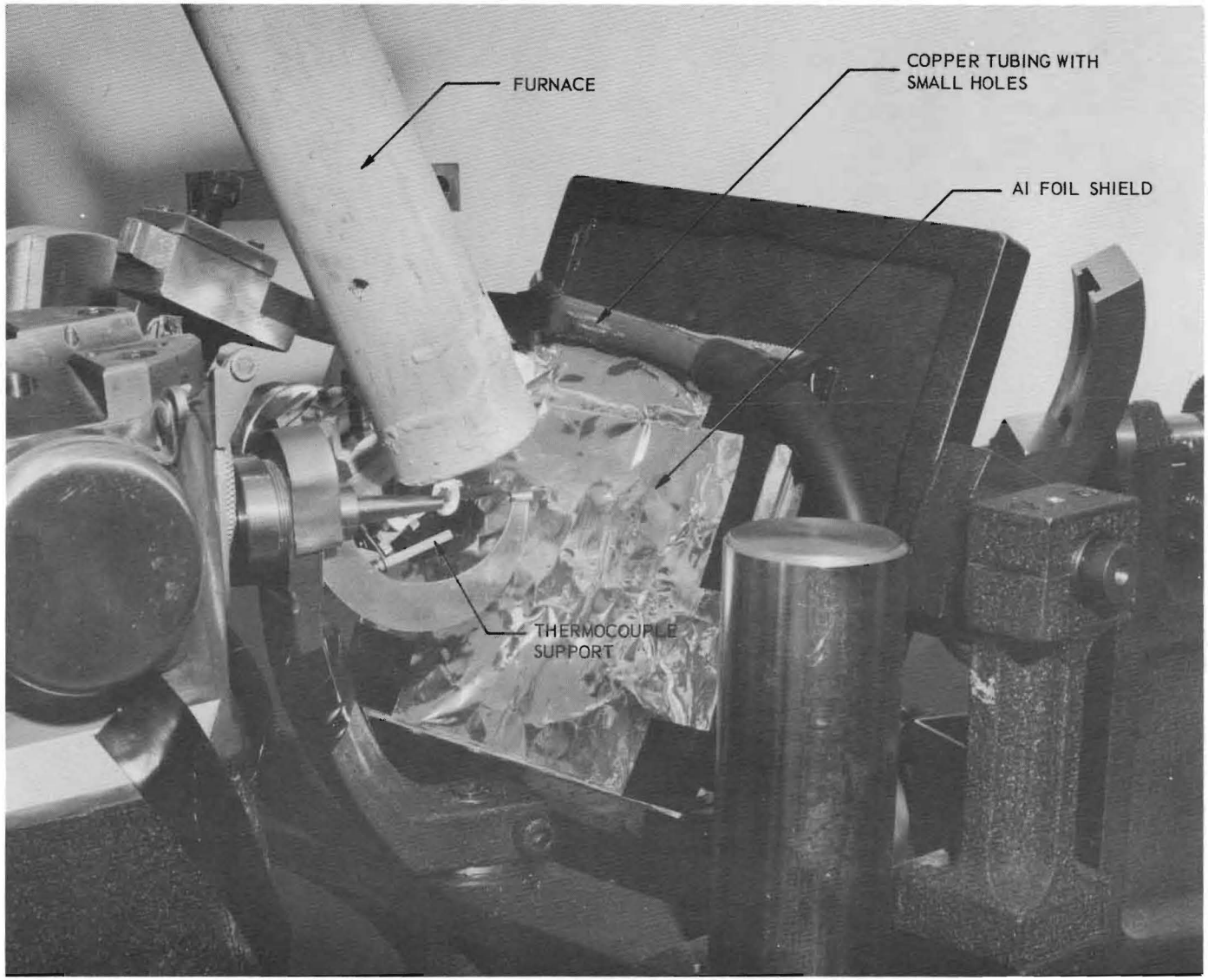

Figure 4. Hot Air Furnace and Film Shield on Precession Camera.

an extensive study of transition temperatures and hysteresis he had established that the transition temperature of this sample was 573.5° C and did not exhibit hysteresis. Monitoring the intensity of a particular reflection as the temperature of specimen #7-A is varied slowly back and forth through the transition temperature makes it possible to associate an indicated temperature with the midpoint of the transition to within about 1° C. (The actual "width" of the transition appears to be about 2.5° C.

This affords a calibration point in the high temperature region with the result that our stated specimen temperature of 600° C, used in collection of the β-structures data, probably represents the actual mean specimen temperature to within less than 5° C.

This calibration procedure is performed for each new thermocouple and periodically with the one currently in use. (It was in part the dependence of apparent transition temperature on thermocouple placement that led to the $\pm$ 1° determination of temperature distribution near the crystal.)

C. Background Intensity

The attempt to see if some off-peak scattering of the K_α radiation was due to TDS, by noting its temperature dependence and behavior at the transition, led to the re-examination and considerable clarification of the whole topic of determination of background intensities. A full discussion of the topic, which is being investigated in part in connection with another (ONR) project, is too extensive to be included here and is as yet not fully written up. Some of the principal results may be pointed out with the help of Figures 5a and 5b. The figures show the results of scanning over the Bragg peak with the first one and then the other member of a pair of balanced filters. The naming of types of scans follows that of Furnas[1]. In the 2 θ-scan (Figure 5a) both the crystal and the counter are rotated, with the usual 1 to 2 angular velocity ratio. In the ω-scan (Figure 5b) the counter is kept stationary while

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[1]Thomas C. Furnas, Single Crystal Orienter Instruction Manual (Direction 12130A) General Electric X-Ray Department, Milwaukee, 1957.

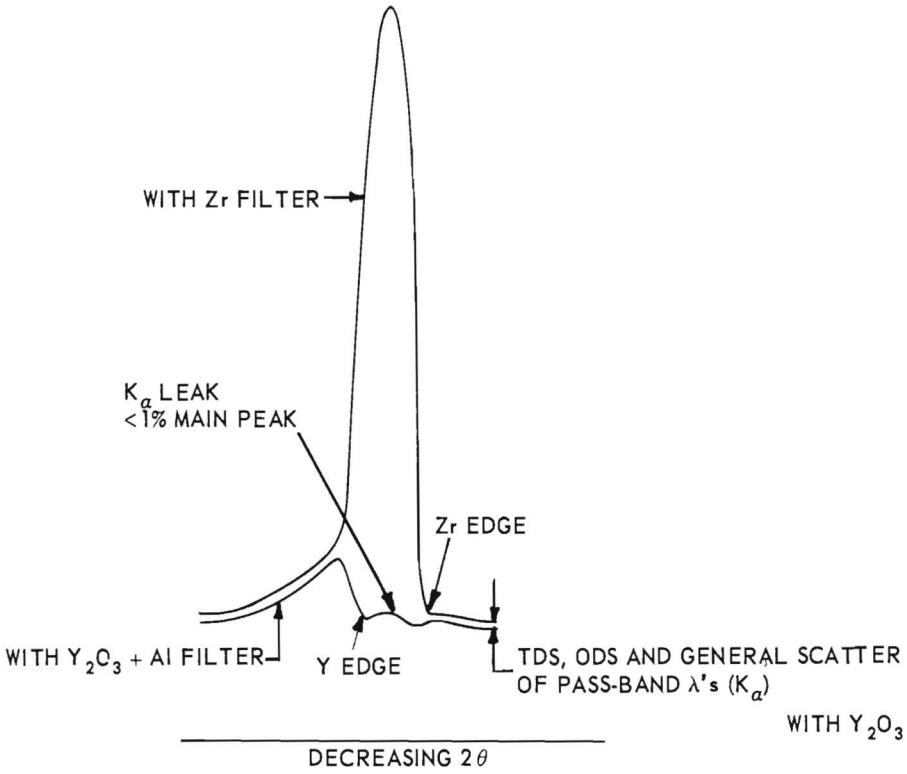
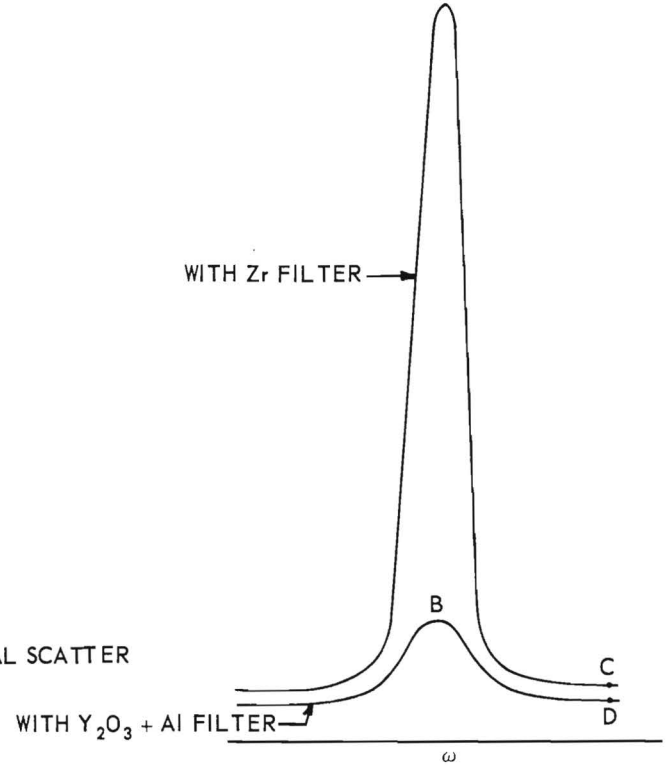


Figure 5a. Typical 2θ-Scan with Balanced Filters.



BACKGROUND COMPONENTS:

C = TDS, ODS, General Scatter from Air, X-tal Surface, Collimator, etc.

C – D = TDS, ODS, and General Scatter of Pass-band λ's (K_α).

D = TDS, ODS, and General Scatter of Non-pass-band λ's.

B = D Plus "Harmonics" from n/λ and λ/n, n usually not integer.

A – B = True Bragg Scattering Plus TDS, ODS, and GS of K_α.

(A – B) – (C – D) = True Bragg Scattering Plus Peaking of TDS.

Figure 5b. Typical ω-Scan with Balanced Filters.

the crystal is rotated through the diffracting position, the counter aperture is made sufficiently wide to accept all Bragg-reflected radiation with wavelength between the absorption edges of the filter pair. In our procedures a scintillation counter is generally used as is a pulse height analyzer set for 90% transmission of the characteristic radiation.

Among other things our investigations have so far enabled us,

(1) to identify various component contributions to the background intensity,

(2) to understand clearly the differences between the 2θ and ω-scan in regard to off-peak measures of background,

(3) to identify as to source and nature and also to measure a sometimes major contribution to the ω-scan background which is entirely missed in the usual method of using off-peak readings alone for background determinations,

(4) to reduce one component of the background by identifying its source and subsequently improving (discussed later) the "collimation" of both incident and detected beams, and

(5) to develop a procedure, based on an understanding of the various components of the background and to what extent they are measured by each of several possible individual measures, for taking advantage of balanced filters plus (necessarily) three different measures (of which two are off-peak) to determine the true background for an ω-scan, excepting for the possible peaking of diffuse scattering under the Bragg peak.

Some of the components are identified in Figure 5b as:

C-D--miscellaneous (non-Bragg) K_α scattering, such as from air and collimators, amorphorous surface layers of specimen, and diffuse scattering

B-D--contribution of harmonic and sub-harmonic wavelengths, plus small amount of Bragg scattered K_α, plus some Bragg scattered wavelengths near but outside of filter pass band.

As the harmonics are contributed by reflection from planes other than the one being investigated, their relative contributions are dependent both on temperature and on the particular Bragg reflection being examined. Because of the effect of dispersion the relative contributions also have an explicit and predictable angular dependence.

It would appear that the only possibly valid measure of background that can be made without the use of balanced filters is the off-peak measure made in a zero-layer 2 θ-scan without crystal monochromatization. (Batterman[2] has demonstrated that major errors may be contributed by even the sub-harmonic contributions to apparent Bragg peaks measured with the double crystal diffractometer technique unless balanced filters are also used.) In all other cases of either ω-scan or 2 θ-scan the use of balanced filters appears to be necessary, pulse height analysis notwithstanding. And, when balanced filters are used it is then necessary to make separate measures of the non-Bragg scattering of the wavelengths in the filter pass-band (this will usually be principally the K_α radiation). The method of using these measures in computing the actual background is discussed in the second paragraph below. Particularly in order to identify the contribution of thermal diffuse scattering (TDS) to the off-peak background measure (and thereby to assess something of the seriousness of neglecting the TDS contribution to the apparent Bragg peak) one might still wish to use a balanced filter technique even with the 2 θ-scan.

Thus it appears that the use of balanced filters is mandatory in precision x-ray Bragg reflection measurement procedures. One wonders how much the lack of appreciation of the various above-mentioned aspects of background measurement has contributed to the final "R-value" in much of the structure work now in the literature, particularly that based on counter data. It is especially notable that the fairly widely used technique of using the off-peak intensity as the background for an ω-scan, such as is suggested by Furnas[1] and has been previously used by many workers (including the present author in a precision refinement of the α-quartz structure[3]), is a particularly invalid method of determining the actual background!

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[2] Boris W. Batterman, paper no. 37 at the Eighteenth Annual Pittsburgh Diffraction Conference, November 9-11 (1960).

[3] R. A. Young and Benjamin Post, "Electron Density and Thermal Effects in Quartz I. Alpha Quartz From 155° K to 300° K" submitted to Acta Crystallographica, based on Ph. D. Dissertation in Physics of R. A. Young, Polytechnic Institute of Brooklyn, (1957) and presented at the American Crystallographic Association meeting at Cornell University July 19-24 (1959).

As an example, the procedure for determining the proper background for the integrated intensity obtained with properly balanced filters by an ω-scan technique is described with reference to Figure 5b and the counter-adapted Weissenberg. Points C and D are at the same ω-setting and are far enough removed from the main peak not to include any of the true Bragg scattering. Experimentally these points are generally chosen to be points where the curves of Figure 5b are essentially flat. The difference in intensities at C and D, I_{CD}, is due to diffuse scattering plus miscellaneous K_α scattering from air, collimators, non-crystalline surface layers on the specimen, etc. In the zero-layer cases so far examined this has proved to be a smooth function of Υ, the counter elevation angle, (which is the same as 2θ in these zero-layer cases). Thus,

(1) it is possible to make a plot of I_{CD} vs Υ, on the basis of a relatively few measures, which may then be used to determine the I_{CD} values appropriate to the various reflections in the particular zero-layer, and

(2) since I_{CD} is a slowly varying function of Υ it may be assumed that its value under the Bragg peak is essentially what it is beside the Bragg peak (note that this is the weakest point in the procedure as the peaking of diffuse scattering--most especially the one-phonon contribution to the thermal diffuse scattering--under the Bragg peak is hereby not measured as a part of the background). The integrated Bragg intensity, $\mathcal{I}$, corrected for background including harmonic contributions but not including the peaking of diffuse scattering under the Bragg peak, is given as follows:

$$\mathcal{I} = \int_{\omega_1}^{\omega_2} I_\beta \, d\omega - \int_{\omega_1}^{\omega_2} I_\alpha \, d\omega - I_{CD} \, \Delta\omega \qquad (1)$$

$$= \mathcal{I}_\beta - \mathcal{I}_\alpha - \mathcal{I}_{CD}$$

where

I_α = the intensity at any point as measured with the low "z" member of the filter pair (which strongly absorbs the K_α radiation) in place.

I_β = the intensity measured with the high "z" member of the filter pair (which is usually known as the "β-filter").

The quantity $\mathcal{I}_c = I_c \Delta\omega$ has often been taken as the background in this type of scan; it is clear that $I_c \Delta\omega$ is in general not equal to $\mathcal{I}_\alpha + \mathcal{I}_{CD}$. Depending on the particular reflections involved, $\mathcal{I}_\alpha$ may be 3/4 $\mathcal{I}_\beta$ or more and will be several times the size of $\mathcal{I}_c$. Thus the neglect of the peaking of I_α under the peak could cause the measure of $\mathcal{I}$ to be in error by a factor of 4 or more. On the other hand, I_{CD} is not generally negligible either, particularly in a poorly collimated system such as is actually desirable, for other reasons, in the use of the ω-scan. Most particularly it is not negligible in the simple peak height (stationary counter, ω set to give maximum value of I_β) technique.

As was pointed out earlier, it was the investigation of the cause of a large I_{CD} which led to the detailed examination of the background intensity. It was at first thought that I_{CD} must represent an unbalance in the filters which had been balanced on the (Norelco high-angle) diffractometer. When a G. E. goniostat (on a GE XRD-5 unit) became available 2 θ-scans were made with the same specimens and filters as were used on the counter-adapted Weissenberg. These showed that I_{CD} differed markedly from one instrument to the other, as might be expected from differences in K_α scattering due to differences in collimation. Subsequent pulse height analysis showed that I_{CD} was indeed due to K_α or nearby wavelengths.

Addition of an improved scatter shield on the end of the collimator and addition of "collimation" of the detected beam greatly reduced the magnitude of I_{CD}.

The "collimation" of the detected beam consists of a pair of pinholes carried (1) by the counter and (2) by an improved counter heat-shield especially made for the purpose. This heat-shield is shown in Figure 2 where the adjusting screws provided for proper centering of the pinhole may also be seen.

Several pairs of pinholes of various sizes have been provided. Each pair is used in the particular range of T (equivalent to 2 θ in the zero-layer) wherein it admits all of the diffracted radiation lying in the filter pass band* but is not a great deal larger than necessary. Hence I_{CD} is not allowed to become inordinately large. Four pairs are now in use to cover the range of T from 0 to 90°.

D. X-Ray Data on β-Quartz

1. Selection of specimens

As was pointed out in the last report (Technical Operating Report No. 6) some selection of specimen material was necessary in order that all specimens from the same parent should give similar results. Variations among sets of relative intensities from various specimens prepared from the same parent crystal are probably due to inhomogeneity of the better formed crystals with respect to perfection and hence in respect to the severity of extinction. Less variation among specimensfrom the same parent is presumed to mean (1) less extinction probably present and (2) a greater likelihood that the extinction will be isotropic and hence correctable by comparison of powder intensity data with single crystal data.

Several specimens from each of a number of parent crystals were examined in the β-phase (at about 600° C) for variations in relative intensities. Variations among specimens from some parent crystals ran as high as a factor of 3 in respect to the ratio of a particular pair of strong and weak reflections, $\frac{(101)}{(003)}$. For Georgia milk quartz the maximum variation in the ratio among 8 specimens was only 10%. Thus, Georgia milk quartz has been selected as the material for which the refined β-structure will first be determined. Enough of the parent material is also available to permit preparation of several powder samples, for which relative intensity data at 600° C are to be collected later. The relative intensities of several specimens were rechecked in the β-phase after from one to ten or more reheatings. None showed any changes (in the β-phase) as a result.

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*Furnas'[1] calculated values of the minimum required aperture size at the counter were helpful in this connection.

Obvious disadvantages of the milk quartz, as opposed to clear quartz, are that (1) it may be less likely to be typical of quartz in general and (2) the apparent temperature factors will almost surely be excessively large due to the very strains and distortions which produce the milky appearance. However,

(1) re-refinement by the present author[3] of the data of Brill, et al.[4] on α-phase milk quartz resulted in coordinate parameters not significantly different from those obtained with clear synthetic quartz[3], even though the (anisotropic) temperature factors were appreciably larger in the least squares refinement of the Brill data, and

(2) even though the temperature factors may be falsely enlarged by static displacements (distortion) the changes that take place in them during the transition would be expected to be much less severely affected by the "milk" vs "clear" differences than are the temperature factors themselves.

As a further check on the suitability of the milk quartz, the transition temperature was compared with that of the particularly well-behaved "Penn State sample" (#7) from Dr. Tuttle's collection (transition temperature 573.5° C as determined by very careful DTA measurements, no hysteresis was found). The transition temperature, as indicated by a thermocouple near the specimen when the x-ray intensity of a particular reflection showed the transition in progress, was the same, within the limitations of the experiment (about 1 to 2° C) for the two specimens.

For the foregoing reasons it is expected that the milk quartz will be a suitable material on which to make the initial determination of the transition mechanism.

2. Single crystal data collection in the β-phase

a. Precession camera data

Some zero-level, (hoℓ), 30° precession photographs have been made in the β-phase at 600° C with MoK_α in order to check on the general appearance of the reciprocal lattice and in particular the regions

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[4] R. Brill, C. Hermann, and Cl. Peters, Ann. Physik 41, 233-44 (1942).

being examined by counter means. The possible contribution of thermal diffuse scattering to apparent Bragg intensities is a point of particular interest here. More such photographs will be made as other specimens and other zones are examined.

b. Counter data

(1) Procedures

The counter data for the β-phase have so far all been collected in the zero-layer at 600° C with MoK_α radiation and with the use of the counter-adapted Weissenberg camera and furnace modified, as described herein, from their condition as described in Technical Note No. 1. Either ω-scan data or stationary counter-stationary crystal (peak height) data constitute practically all of the counter data so far collected.

The data finally derived are relative integrated intensities. However, only enough integrated intensities are actually measured to establish the relationship between integrated intensities, $\mathcal{I}$, as given by Equation 1 and peak height, I_{max}, as given by

$$I_{max} = I_A - I_B - I_{CD} \qquad (2)$$

Integrated intensity data are required for enough reflections (~ every 5° in Υ) to establish a plot of the quantity

$$B_o = \frac{\mathcal{I}}{I_{max}} \qquad (3)$$

as a function of 2 θ for each crystal and each set of apertures used. Only peak height (I_{max}) data are collected for the remaining reflections.

Temperature readings are made several times during the time taken to collect data on any one reflection.

The various sets of apertures are used for different ranges of T as was previously explained. In each T range certain reflections are chosen as "standards" and are remeasured periodically during the course of any data collection period. This procedure provides a continuing check on the overall stability of the equipment and would give warning of gross misalignment of the crystal if it should occur. The full alignment procedure is carried out at least once each day (at temperature). The early troubles with specimen twisting on heating have been completely overcome; it is usual that no discernible change takes place in the crystal alignment for days on end, even though the crystal goes through many cycles of heating from room temperature to 600° C.

At least 3 reflections, which have T values common to two aperture ranges, are measured as a part of both ranges. The combination of periodic checking of standard reflections in each range and this double collection of data in the "overlap" region between ranges allows all intensity data in all ranges of T and from all data collection periods to be brought to a common scale.

(2) Results

Full sets of {hoℓ} counter data out to the (209) have been collected at 600° C from each of two different specimens, 4H and 4I, of Georgia milk quartz. By "full" is meant all of the data, background and otherwise, required to yield on a common scale the relative integrated intensities in the Bragg peaks. The sets of relative intensities from the two crystals are generally in good agreement; individual discrepancies are now being investigated. The collection of {hk0} β-phase data (at 600° C) on another milk quartz specimen (4J) is underway. Of particular interest in connection with the discussion of the background problem are the ω-scans made to determine integrated intensities directly. These show graphically a number of the points brought into focus in the recent re-study of the background problem. These include (1) the dependence of $I_B - I_D$ (see Figure 5b) on T, on the particular reflection, and on the aperture system used, (2) the dependence of I_{CD} on aperture system and T, and (3) the importance of the proper collection and treatment of background intensity data as discussed in this report.

One zero-level, {hoℓ} zone precession picture was also made of each of the specimens 4H and 4I (Georgia milk quartz) at 600° C. No pronounced TDS and no unusual character in the appearance of the reflections were evident.

3. Data reduction

The data reduction procedures are implied by the foregoing but (for clarity) are explicitly stated here in stepwise fashion:

a. Reduce gross peak height data (I_A) to true peak heights (I_{max}) by use of equation (2). (I_{CD} may be obtained from plots of I_{CD} vs Υ made for each crystal and each aperture system.)

b. Prepare B_o vs θ plots for each crystal from ω-scan integrated intensity data using Equation (1) to correct for background.

c. Bring all data on each crystal to a common scale by making use of measurements of "standard" reflections and the reflections measured in the overlap regions of the various aperture systems.

d. Convert each peak height (I_{max}) to the corresponding integrated intensity, $\mathcal{I}$, by use of the B_o vs Υ plot for the particular crystal.

e. Apply Lorentz and polarization (LP) factors and absorption factor if required. The absorption corrections calculated by Evans and Eckstein[5] for spherical crystals are to be used here, but so far ($\theta < 45°$, $\mu R < \sim 0.2$) the indicated correction has amounted to much less than 1% and has therefore not been applied.

f. Apply extinction corrections. These have yet to be determined. We do not have the equipment to allow use of Chandreskhar's method[6], which would presumably yield the best available corrections. Since the time and money are not available on the present project for building such equipment an approximate, isotropic extinction correction will be made by comparison of the single crystal data with powder data. Equipment is on hand for collecting the necessary high temperature (600° C) powder data.

- - - - -

[5] H. Evans and Miriam Eckstein, Acta. Cryst. 5, 540-2 (1952).

[6] S. Chandrasekhar, Acta. Cryst. 13, 588 (August 1960).

The above procedure will result in our best estimate of relative $|F_{hk\ell}|^2$ values. No corrections for peaking of TDS under the Bragg peaks are presently contemplated. (Note that the TDS contribution is partially corrected for by the background measurement I_{CD} of Figure 5b.)

IV. FUTURE WORK

As currently visualized, the program for bringing the studies to some conclusion under the present contract, which now has three quarters to run, is approximately as follows:

Dauphiné twinning and extinction are the biggest problems. The goal is to determine the progress of both coordinate and thermal parameters as the crystal goes through the transition.

The problem of extinction is being met first by choosing specimens (milk quartz) which are relatively homogeneous in respect to extinction and in which the effect is, for quartz, relatively small. Second, approximate extinction corrections will be made on the basis of comparison of powder data with single crystal data. Third, in the analyses relatively more emphasis will be placed on the weaker reflections which exhibit relatively less of the extinction effect. It is recognized that this procedure is not a wholly satisfactory method of dealing with extinction. It is felt, however, that the procedure outlined is an appropriate compromise between effort and accuracy under the circunstances.

The problem of Dauphiné twinning has been found to be especially severe because of the easy and unpredictable variability of the amount of such twinning present in any one crystal. This problem is being met by concentrating on the β-phase, where Dauphiné twinning does not occur, and on the {hk0} and {hhℓ} type reflections as they are not effected by this type of twinning.

The {h0ℓ} zone contains all of the parameters, the {hk0} zone does not contain the z-coordinate of the oxygen nor any of the thermal parameters (i.e., components of the anisotopic temperature factors written as second order tensors) which have components in the z-direction. It is planned that {h0ℓ} data will be used to refine the 600° C β-structure first. {hk0} data,

also at 600° C, will then be used to refine those parameters which occur in this zone and the results from the two types of data will be compared. {hhℓ} data will then be used to determine the parameters which have z components, though these will not be as well determined as they will be in the refinement of the {hOℓ} data because fewer data will be used.

The comparison of {hOℓ} results with {hkO} plus {hhℓ} results at 600° C is considered desirable for 3 reasons:

(1) the two sets of data represent different "views" of the crystal structure,

(2) some as yet unexplained discrepancies were found in comparing {hOℓ} and {hkO} results in the author's previous refinement of α-quartz (though now that both the background contribution and the behavior of Dauphiné twinning are better understood it is suspected that the data may be in error somewhat due to both of these causes and that perhaps the discrepancies may be so explained), and

(3) since this is to be the reference structure in the determination of the transition mechanism it is well to have it more overdetermined than would otherwise be necessary.

The intensities of the {hkO} and {hhℓ} reflections will then be followed as a function of temperature through the transition. This should make it possible to determine (1) the structure in the α-phase just below the transition, (2) the structure in the β-phase just above the transition, and (3) most importantly, the changes that take place in the structure at the transition. It is particularly to be noted that the changes in the structures will probably be more reliably determined than are the structures themselves. A point of difficulty, of course, will be the smallness of the number of {hhℓ} data on which all determinations of changes along the z direction (parallel to the c-axis) must be based.

To the extent that time permits the investigation with {hkO} and {hhℓ} data will be continued down from the transition temperature to 50 or 100° C below the transition, in which range many physical properties display rapid changes with temperature.

It would undoubtedly be of great interest to investigate the occurrence at the transition of "spikes" in the intensity vs temperature data from reflections that are affected by Dauphiné twinning. It seems clear now, however, that it will not be possible to make such investigations as a part of the present contract; additional support for the purpose may be sought later.

As pointed out above, 600° C {hoℓ} data for two crystals are now on hand. The collection of {hk0} data has been started. During the next quarter it is expected that {hk0} and {hhℓ} data at 600° C will be collected for two specimen of milk quartz and the collection of I vs T data for these reflections will be well started. In addition, powder data* at 600° C will be collected, the extinction corrections based on these data will be obtained and applied to the existing {h0ℓ} data. Refinement procedures, both least squares and Fourier (electron density map), will be undertaken with the {h0ℓ} data.

In subsequent quarters, after the data have been collected on the #4 specimen and analyses are well underway, portions of similar data will be collected with crystals from other sources for comparison purposes. It is expected that crystal-to-crystal variations will be found (1) in the strong reflections (which are generally "close in") because of differences in extinction and (2) in the "far out" reflections (which are generally weak reflections) because of differences in strain. The most fruitful course to follow in making comparisons of structures and transition mechanisms on the basis of relatively few data is therefore not immediately apparent.

V. PERSONNEL

Messrs. Jude H. Koenig and N. Kelly Hearn, Assistant Research Physicists, and Mr. W. A. Stephens, Student Assistant (Freshman in Physics), have each contributed notably to the success of the project during the past quarter. Each is due special commendation for his interested and enthusiastic efforts: Mr. Hearn in connection with the mechanical problems; Mr. Stephens in connection with crystal mounting and alignment and in connection with intelligent

and rapid data collection; and Mr. Koenig in connection with organizing, overseeing, and taking part in the work on the various aspects of equipment modifications and data collection and in connection with recognition of and solution or help in solution of many of the problems concerning reliability and precision in the final intensity data. Again it is noted that Mr. Stephens' achievements are particularly remarkable in view of his youth (18 years), formal educational level, and very limited scientific work experience.

Necessary changes in assignments within the laboratory have resulted in the complete re-assignment of Mr. Hearn to other projects. For a time, at least, Miss Roxana Speight (Research Assistant mentioned in previous reports) will devote about 50% of her time to the project. Mr. Koenig will devote about 50 to 60% of his time and Mr. Stephens will continue to work about 25 to 30% time.

VI. BUDGETING AND ADMINISTRATIVE MATTERS

Approximately $17,500 was left in the contract budget as of 31 December 1960.

The 6 month no-cost extension previously discussed has been granted. The remaining funds are expected to be adequate to bring to fruitful conclusion a suitable portion of the work undertaken. Support for investigation of questions raised but left unanswered during the course of the present work and of other extensions or refinements of the present studies will be sought either separately or in a renewal proposal.

Respectfully submitted,

R. A. Young
Project Director

Approved:

Vernon Crawford
Head, Physics Branch
Physical Sciences Division

TECHNICAL OPERATING REPORT NO. 8
Project No. A-447

MECHANISM OF THE PHASE TRANSITION IN QUARTZ

By

R. A. Young

Contract No. AF 49(638)-624

Air Force Office of Scientific Research
Washington 25, D. C.

April 1, 1961

Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

MECHANISM OF THE PHASE TRANSITION IN QUARTZ

Technical Operating Report No. 8

Period Covered: 1 January through 31 March 1961

Contract No. AF 49(638)-624
(Project A-447)

April 1, 1961

R. A. Young
Project Director

Air Force Office of Scientific Research
Washington 25, D. C.

Technical Operating Report No. 8, Project A-447

January 1 through March 31, 1961

I. TITLE

Mechanism of the Phase Transition in Quartz

II. OBJECTIVE AND SCOPE

The central objective of this study is the determination of the mechanism of the phase transition in quartz. An x-ray diffraction method is to be used; the mechanism is to be described in terms of the changes that occur in the equilibrium positions and thermal vibrations (thermal ellipsoids) of the atoms as the crystal undergoes the transition at about 573° C. The study is to entail first refining either the α- or β-structure at a temperature near the transition temperature used. The temperature dependences of selected Bragg intensities, measured individually as continuous functions of temperature, will then be used to establish the atomic positional and vibrational changes that take place as the crystal temperature is varied to and through the transition temperature. Precision measures of intensities and changes in intensities (and of structure amplitudes) are emphasized. Nearly all quantitative data will be collected with the use of a counter-adapted Weissenberg camera provided with a flexible, controllable ($\pm$ 3° C or better) hot air furnace. Various features of the technique, measurements made, sources of error considered, and handling of the data reflect the effort to obtain precision.

Refinements and other analysis procedures will include both a least squares approach (using individual, anisotropic temperature factors) and Fourier synthesis (electron density and Patterson maps) methods.

A variety of specimens is to be included in the study in order that the results may be applicable to "quartz" rather than only to a particular sample.

As time permits, the studies of changes in coordinate and thermal parameters will be extended to cover the 100° C or so region just below the transition in order that correlations may be attempted with the marked changes in various physical properties which occur in this region.

III. CURRENT STATUS

Satisfactory progress has been made during the quarter toward the ultimate goal of defining the mechanism of the $\alpha \rightleftarrows \beta$ transition in quartz. The general plan of attack is still to determine a refined structure of β quartz at 600° C and then to investigate the transition mechanism with the temperature dependences, over the range 450° C to 650° C, of those x-ray reflections not affected by Dauphiné twinning. All of the equipment, including especially the hot air furnace, has been working very well for several months. The several aspects of the progress made and ancillary investigations are treated separately.

Extinction

Extinction has been mentioned repeatedly in the past as presenting one of the major experimental obstacles. We have been working with milk quartz for some time now in order to minimize the effects of extinction on our initial determinations of structure and mechanism.

It was stated in the last Technical Operating Report that the 600° C single crystal relative intensities were to be compared with 600° C relative intensities of powdered material prepared from the same parent crystal. This has now been done for several sets of data with the results that (1) the standard deviation in the powder data, as determined by repeated measurements, appeared to be no better than about 6.5% (due principally to uncertainties in background placement), (2) only 5 lines in the powder pattern at 600° C were sufficiently strong and well-resolved to allow good measurement, and (3) within the experimental errors determined by conditions (1) and (2), a plot of $\frac{|F|^2_{\text{single crystal}}}{|F|^2_{\text{powder}}}$ vs $|F|^2$ powder (Figure 1) showed no trend with $|F|^2$ and all points fell within ±10% of a horizontal straight line. It was therefore concluded that no extinction was indicated by the comparison.

An interesting observation concerning secondary extinction (and, by implication, probably primary extinction as well) was made by comparing the B_o's (ratios of integrated intensity to peak intensity) and integrated intensities of two milk quartz specimens, 4H and 4I. The B_o's of 4H were consistently a little more than 2-1/2 times the B_o's of 4I, yet the relative integrated intensities

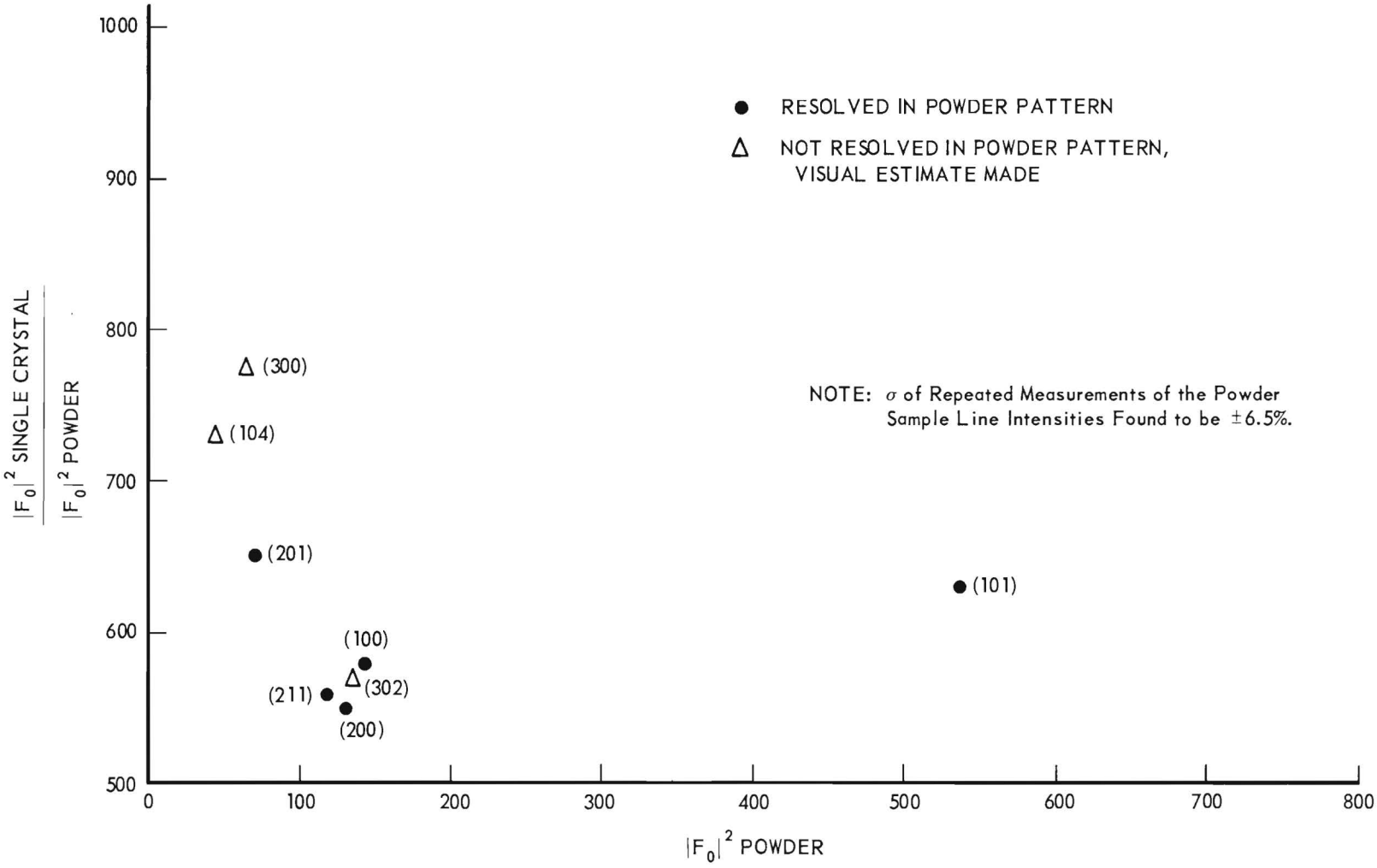


Figure 1. Comparison of Single Crystal and Powder Intensities.

were very much the same for the two crystals and did not show any trend with $|F|^2$, as is indicated by figure 2 (most of the largest $|F|$ values occur at the smaller 2θ values). Since identical ω-scan techniques were used for collecting the two sets of data, the differences in B_o indicates a considerable difference in the mosaic spread in the two crystals. The lack of effect of mosaic spread differences on relative intensities is strong evidence that secondary extinction is not present to any significant degree.

It therefore appears that the choice of the present milk quartz specimens has largely overcome the problems that might otherwise have been presented by either primary or secondary extinction or the combination of the two.

Data Collection

The primary data collected, particularly when data are collected as a continuous function of temperature, are peak intensities. Direct integrated intensity (total count) data and other data relating to B_o are necessarily collected at intervals to assure that all peak intensity data may be correctly transformed to integrated intensity data. Additional continuing checks are required on such things as reproducibility, limits of observability, the performance of the various parts of the apparatus, and the adequacy of the (counter) aperture system used. The collection of a set of acceptable (by our standards) integrated intensity data from even one crystal at one temperature is quite time consuming, in spite of the admirable performance of our equipment of late. However, due largely to the efforts of Mr. Koenig, considerable new data have been collected during the past quarter. These include (in addition to the 600° C powder data mentioned earlier) the following:

1. Integrated intensity data at 600° C have been collected for the 15 (hk0) reflections observable from each of two milk-quartz crystals of about 1/4 mm diameter (4J and 4K). Larger crystals will have to be employed if more reflections are to be observed. At present we estimate that we have observed all reflections (of the zones examined) for which $|F|$ is 1/300 of the largest $|F|$.

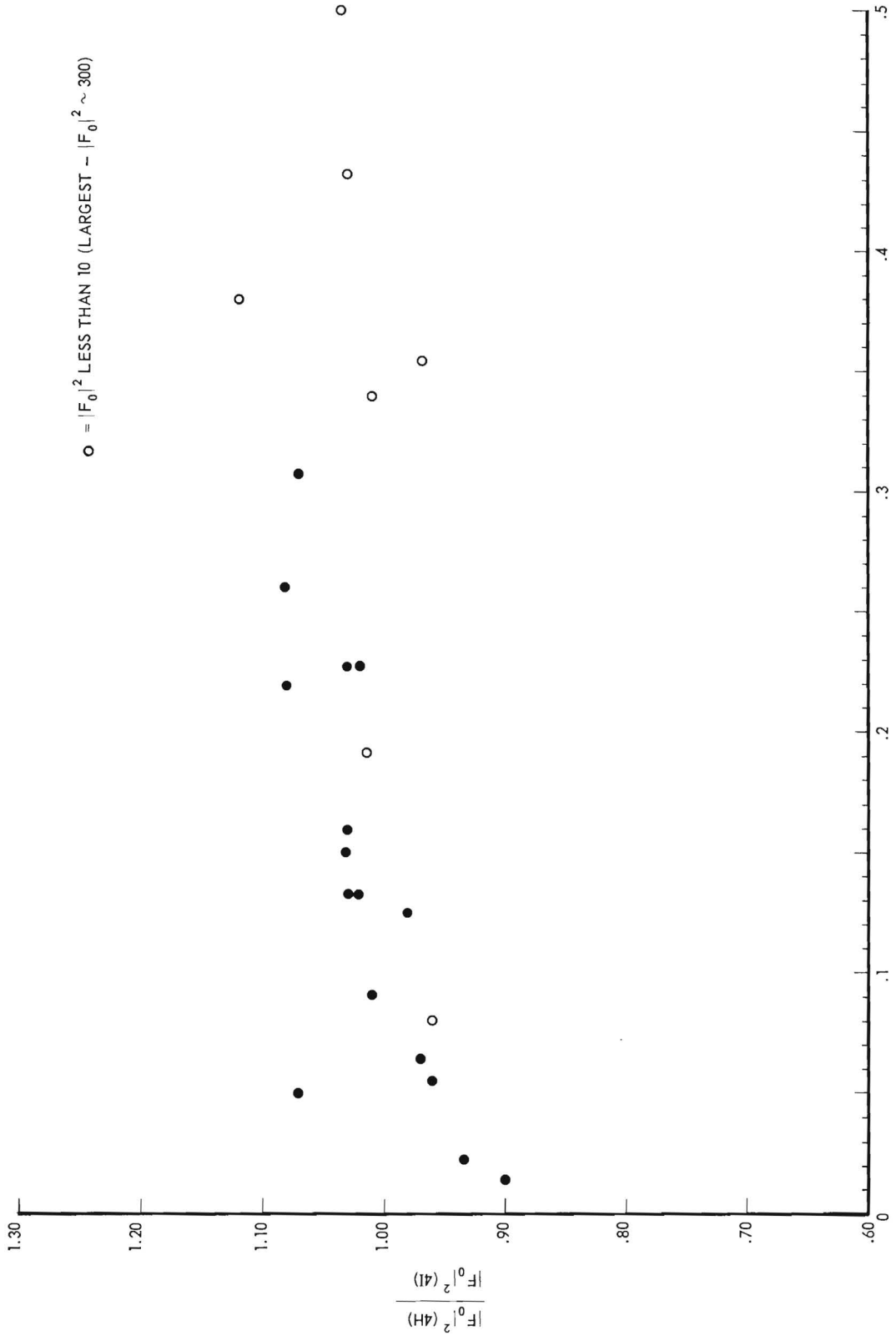


Figure 2. Dependence of $\frac{|F_o|^2\ (4H)}{|F_c|^2\ (4I)}$ Versus $\sin^2\theta/\lambda^2$.

2. The temperature dependences of the integrated intensities of a total of 28 (hhℓ) and (hk0) type reflections (which are the types not affected by Dauphiné twinning) from two crystals (4H and 4J) have been measured from 450° C to 650° C. A number of these (measured) data are shown in figure 3. Something of the reproducibility in these data is indicated by figure 4. It is interesting to note that some things about the temperature induced changes in the crystal may be inferred directly from figure 3 (with the help of a model of the structure). For example, the behavior of the (00ℓ) reflections clearly imply the continuous change of the oxygen Z-coordinate from its value of 0.118 at room temperature to 0.167 (i.e., 1/6) at the transitions. This in turn implies a continuous (with changing temperature) rotation of the SiO_4 tetrahedra of which the structure is composed.

3. A number of data have been collected on the behavior of the B_o's (diffraction profile breadths) as a function of several parameters such as temperature, phase transition, crystallographic direction (in order to assess possible anisotropy in the mosaic spread) and reproducibility as a function of measurement method (i.e., integral breadth as opposed to breadth at half maximum).
The reproducibility of our integrated intensities seemsto be only about 2 to 3%. The ratios of the $|F_{obs}|^2$ values for two crystals shown in figure 2 indicate a standard deviation in $|F_{obs}|^2$ no smaller than about 4%. We felt that the design and conduct of our experiment was generally such that our reproducibility should be better than this and that in particular the reproducibility in measuring a single strong reflection should be 1% or better. It appears that much of our present σ may come from our direct measures of total counts associated with a Bragg peak (on which our B_o vs θ curves are based). We are therefore re-examining the functioning of our spindle drive system, among other things.

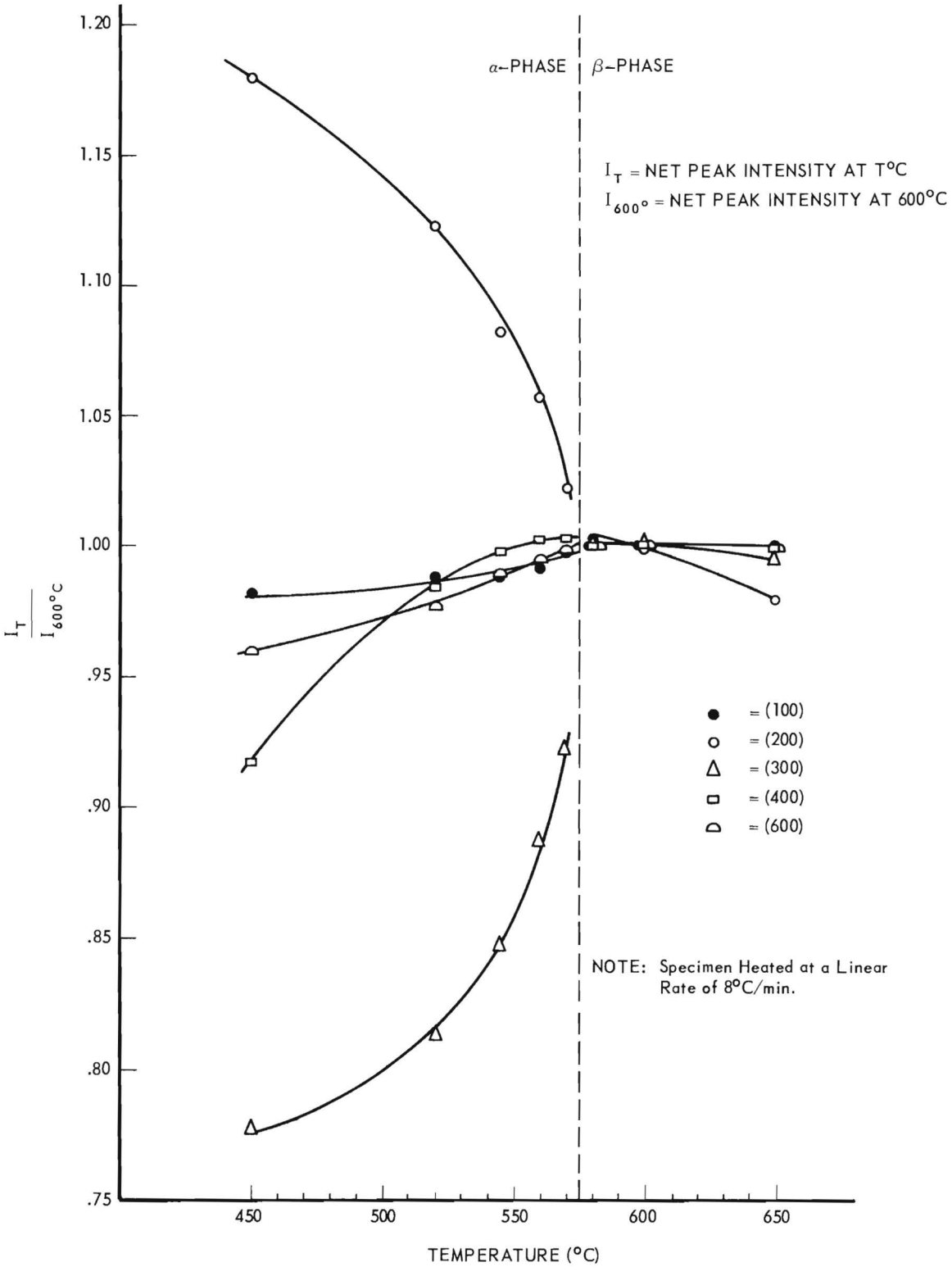


Figure 3a. Temperature Dependence of Peak Intensities, Specimen 4-H (hoo) Reflections.

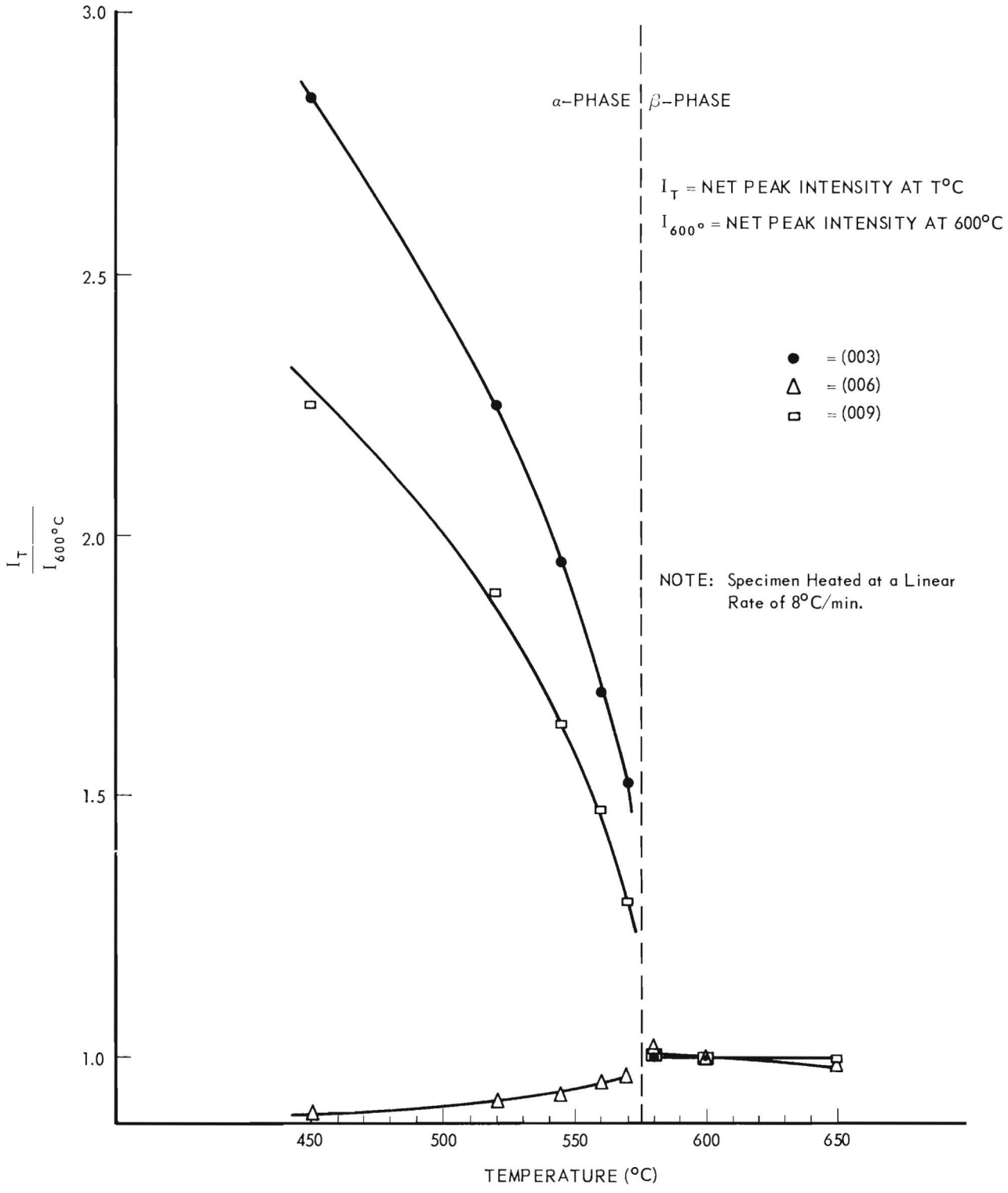


Figure 3b. Temperature Dependence of Peak Intensities, Specimen 4-H (ooℓ) Reflections.

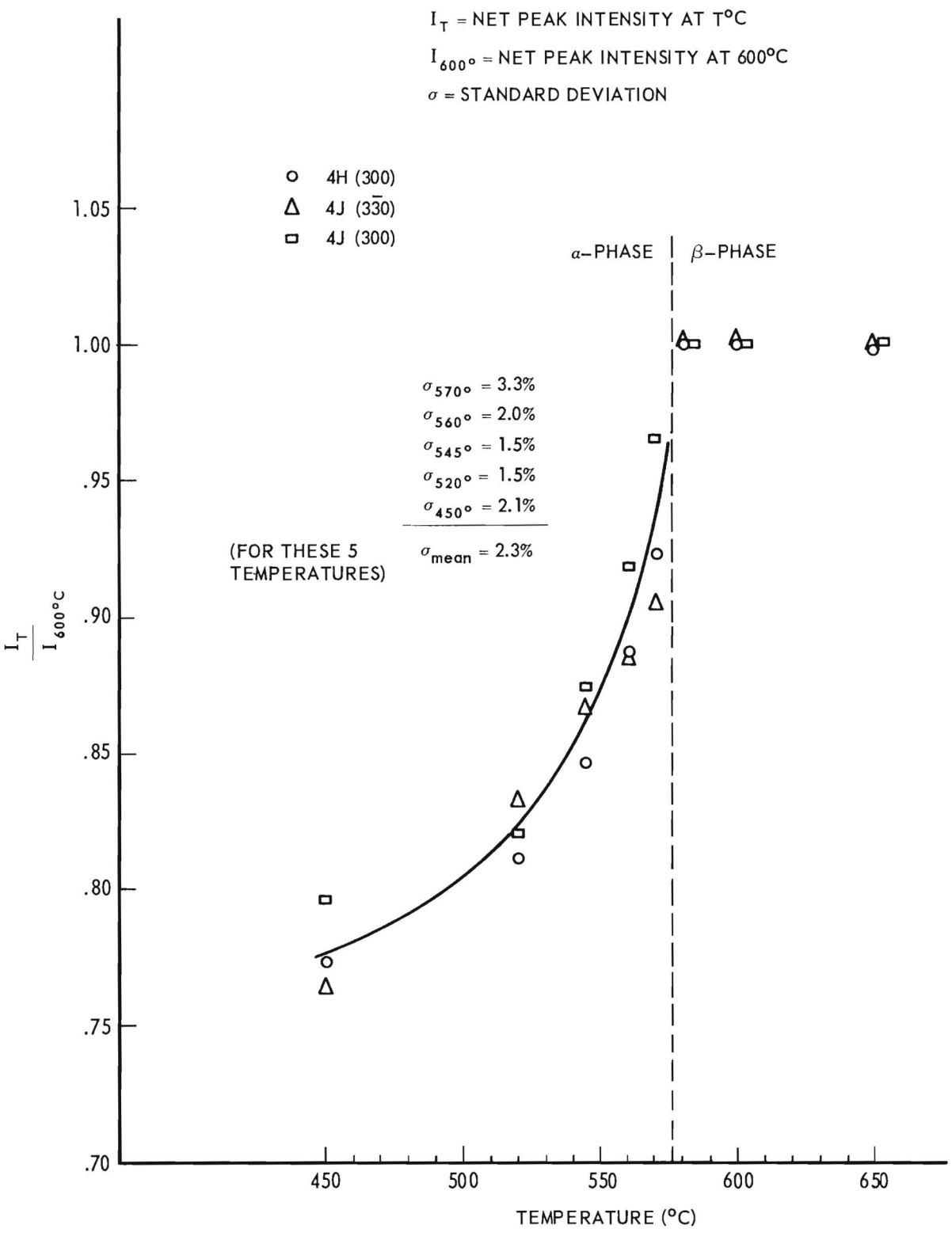


Figure 4. Reproducibility of Temperature Dependence, Three Equivalent Reflections Measured with Two Samples.

Computational Procedures

Arrangements have been made with the National Bureau of Standards to make use of their IBM 704 computer facility. Dr. Helen Ondik and Mr. Al Perloff of NBS are supervising the computation and are writing the necessary special patches for the Busing IBM 704 crystallographic least squares program. Their help is particularly valuable and appreciated. It has been decided that all of the least squares refinement will be based on the symmetry of the space group $P3_22$ even though, in the β-phase, quartz has the higher symmetry of $P6_422$. The purpose of using $P3_22$ throughout is to assure identical treatment of the data above and below the transition.

As a test case a set of room temperature (h0ℓ) data is being used which was previously subjected to least squares refinements on the ORACLE computer at Oak Ridge National Laboratories. Those refinements were carried out, on behalf of the present author, by Dr. Busing with the use of the "Busing and Levy" program before it was re-written for the IBM 704. The results from the two machines are therefore expected to be strictly comparable.

When the test case is satisfactorily completed, computations will be made on a set of 600° C (h0ℓ) data now in the hands of the NBS group. Further sets of data will be supplied to them in the near future.

Dauphiné Twinning

As has been pointed out in past reports we have now designed our experiments to avoid the direct influence of Dauphiné twinning on those x-ray data on which our study of the phase transition mechanism are based. However, this type of twinning continues to interest us (1) for itself, (2) for its possible intimate relation to the phase transition, (3) for its possible role in the explanation of the steep, marked, generally reversible rise in certain Bragg intensities just below the transition temperature, and (4) for the possibility that with further understanding of the behavior and the causes of occurence of Dauphiné twinning we may yet be able to obtain an untwinnable specimen. During the past quarter a portion of our attention has therefore been directed toward further investigation of the literature and a few simple experiments on this

type of twinning. Mr. Koenig will give a paper on the subject on April 29 at the Georgia Academy of Sciences annual meeting. The abstract of the paper is appended to this report. The full manuscript will be included in the next technical operating report. Further discussion of our studies of Dauphiné twinning will therefore await that preparation of that report.

IV. FUTURE WORK

X-ray intensity data will continue to be collected as a function of temperature, first to fill out two sets of (hk0) and (hhℓ) data on milk quartz and then to compare the behavior of other quartz specimens. The severity of extinction in quartz crystals will be assessed to some degree. Further attempts to improve the precision in relative $|F|^2$ values will be made. Some additional 600° C data on milk quartz may be collected in order to improve the standard deviation in the thermal and coordinate parameter determined further temperature.

Some further work related to Dauphiné twinning will probably be carried out. As time permits the intensities of certain reflections which <u>are</u> affected by Dauphiné twinning will be examined as a function of temperature. The (301) and ($30\bar{1}$) reflections are a particularly interesting pair. There is some indication that, because of a possible intimate relation between extensive Dauphiné twinning and the production of the β-phase, the behavior of (h0ℓ) and (h0$\bar{\ell}$) pairs at and near the transition may shed particular light on the nature of the transition.

It is expected that during the next quarter the most interesting progress will be the collection and interpretation of the least squares refinement results for positional and thermal parameters at each of several temperatures between 450° C and 650° C. It is also anticipated that some Patterson maps will be constructed for each of several temperatures. (The (hk0) zone is unaffected by Dauphiné twinning and hence may be followed through the transition.) Of particular interest will be the question of the location and thermal motion of the silicon atom in the β-phase, for example "does it vibrate between two minima in its potential energy field?" This is a particularly interesting

question in view of the existence of double configurational potential minima for many ferroelectrics below their Curie points. The Dauphiné twins in quartz appear to represent just such a case of double configurational potential minima which are no longer distinguishable above a definite transition temperature.

V. PERSONNEL

No personnel assignment changes have been made during the quarter.

VI. BUDGETING AND ADMINISTRATIVE MATTERS

Approximately $14,500 was left in the contract budget as of 31 March 1961. It is expected that these funds will be sufficient with which to conclude the project.

Respectfully submitted,

R. A. Young
Project Director

Approved:

Vernon Crawford
Head, Physics Branch
Physical Sciences Division

APPENDIX A

ABSTRACT OF PAPER FOR GEORGIA ACADEMY OF SCIENCES MEETING, 28 APRIL 1961

X-ray Studies of Dauphiné Twinning in Quartz

JUDE H. KOENIG AND R. A. YOUNG

Engineering Experiment Station, Georgia Institute of Technology

Dauphiné twinning, which amounts to an 180° rotation of the twin about the c-axis, cannot be observed by ordinary polarizing-optics methods. Specular reflection from properly etched surfaces may show up twin boundaries which intersect the surface of the crystal. Certain x-ray reflections are affected, some profoundly, by the presence of these twins whether or not they either intersect the surface or are of macroscopic size.

An x-ray method making use of this effect has been employed in a preliminary study of several aspects of the occurrence of Dauphiné twinning. The method will be described. Some of the effects on Dauphiné twinning of thermal cycling will be discussed and evidence for the possible occurrence of microscopic or submicroscopic twinning will be presented. The significance of such twinning behavior to piezoelectric applications and to crystal structure studies will be mentioned.

20 minutes

3-1/4 x 4 slides

TECHNICAL OPERATING REPORT NO. 9
Project No. A-447

MECHANISM OF THE PHASE TRANSITION IN QUARTZ

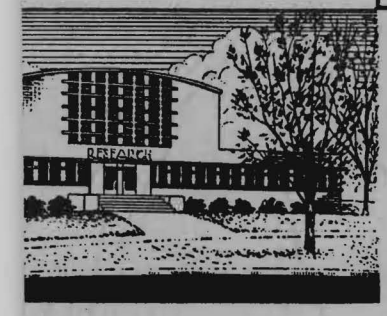
By

R. A. Young

Contract No. AF 49(638)-624

Air Force Office of Scientific Research
Washington 25, D. C.

August 17, 1961



Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

MECHANISM OF THE PHASE TRANSITION IN QUARTZ

Technical Operating Report No. 9

Period Covered: 1 April through 30 June 1961

Contract No. AF 49(638)-624
(Project A-447)

August 17, 1961

R. A. Young
Project Director

Air Force Office of Scientific Research
Washington 25, D. C.

Technical Operating Report No. 9, Project A-447

1 April through 30 June 1961

I. TITLE

Mechanism of the Phase Transition in Quartz

II. OBJECTIVE AND SCOPE

The central objective of this study is the determination of the mechanism of the phase transition in quartz. An x-ray diffraction method is to be used; the mechanism is to be described in terms of the changes that occur in the equilibrium positions and thermal vibrations (thermal ellipsoids) of the atoms as the crystal undergoes the transition at about 573° C. The study is to entail first refining either the α- or β-structure at a temperature near the transition temperature used. The temperature dependences of selected Bragg intensities, measured individually as continuous functions of temperature, will then be used to establish the atomic positional and vibrational changes that take place as the crystal temperature is varied to and through the transition temperature. Precision measures of intensities and changes in intensities (and of structure amplitudes) are emphasized. Nearly all quantitative data will be collected with the use of a counter-adapted Weissenberg camera provided with a flexible, controllable ($\pm$ 3° C or better) hot air furnace. Various features of the technique, measurements made, sources of error considered, and handling of the data reflect the effort to obtain precision.

Refinements and other analysis procedures will include both a least squares approach (using individual, anisotropic temperature factors) and Fourier synthesis (electron density and Patterson maps) methods.

A variety of specimens is to be included in the study in order that the results may be applicable to "quartz" rather than only to a particular sample.

As time permits, the studies of changes in coordinate and thermal parameters will be extended to cover the range 100° C or so below the transition in order that correlations may be attempted with the marked changes in various physical properties which occur in this region.

III. CURRENT STATUS

Satisfactory progress has been made during the quarter toward the goal of defining the mechanism of the a $\overleftarrow{\rightarrow}$ β transition in quartz. The general plan of attack is still to determine a refined structure of β quartz at 600° C and then to investigate the transition mechanism with the temperature dependences, over the range 450° C to 650° C, of those x-ray reflections not affected by Dauphiné twinning. All of the equipment continues to work very well. The several aspects of the progress made are treated separately.

Data Collection

A modification in the procedure for collecting relative intensity data has improved our precision by about a factor of two. We had been trying to use the "peak-height method," which entails measurement of peak-heights and subsequent conversion of these data to integrated intensities on the basis of a previously determined experimental curve of the ratio of integrated area to peak height as a function of diffracting angle. However, it was found that there is sufficient anisotropy in the mosaic spread of our crystals so that the peak height intensities of equivalent reflections vary by ± 5% whereas the full integrated intensities (obtained by ω-scan procedures with correct use of balanced filters, as described in the last report) gave variations of < 2%. It turns out that complete ω-scans with balanced filters can be systematically made in such a way that the necessary three measurements of background are all made relatively expeditiously. Yet the total time involved in collecting a set of such ω-scan data is little, if any, more than the time involved in collecting peak height data and preparing the calibration curve (ratio of area to peak height as a function of angle) required for them.

An automatic mechanism to oscillate the crystal slowly through a very small angular range, which includes the very top of the Bragg peak, has been found very helpful in the collection of intensity-versus-temperature data. Since the ratio of area to peak height for a given reflection generally does not change with temperature, it is ordinarily necessary to follow only the peak height in order to know the behavior of the integrated intensity as a function of temperature. Because of thermal expansion, the position of the Bragg maximum

does change slightly with temperature and it is therefore necessary continually to re-optimize the crystal position in order to stay "on the peak." The continual oscillation through the optimum position makes it possible to observe the correctly optimized peak intensities at closely spaced intervals without any question of the validity of the optimization.

Additional relative intensity data were collected on milk-quartz crystals at 600° C. A crystal somewhat larger than those previously used was employed for the collection of additional (h0ℓ) reflections at this temperature. Additional counter data were collected concerning the (hk0) and (hhℓ) intensities of several specimens as a function of temperature. In addition a systematic survey of the (hk0), (hhℓ), and (h0ℓ) zones of several crystals in both the α- and β-phases was started with the precession camera.

Analyses and Results

Preliminary thermal and coordinate parameter results for β-quartz at 600° C have now been obtained from the National Bureau of Standards IBM 704 computer. Busing's least squares program was used. The results are not surprising but are helpful. For both silicon and oxygen atoms, individually, the major axis of the best single thermal ellipsoid is oriented along the line joining the two possible α-phase positions for each atom. We are not yet able to tell if a double configurational potential minimum actually exists, however. Perhaps the more and better data which are being collected will make it possible, with the help of certain computational tricks, to make this determination; perhaps they will not.

Work has been started on preparation of Patterson maps as a function of temperature but no results have yet been obtained. Our interest in the Patterson maps is in part related to the possibilities of determining whether or not a double configurational potential minimum actually exists in the β-phase.

The intensity-*versus*-temperature data on individual reflections seem quite promising and may help us decide finally about the double minimum question. In any event, these data may possibly point up an intimate connection of Dauphiné twinning with the transition mechanism. We shall dwell on this point a bit with the help of Figure 1.

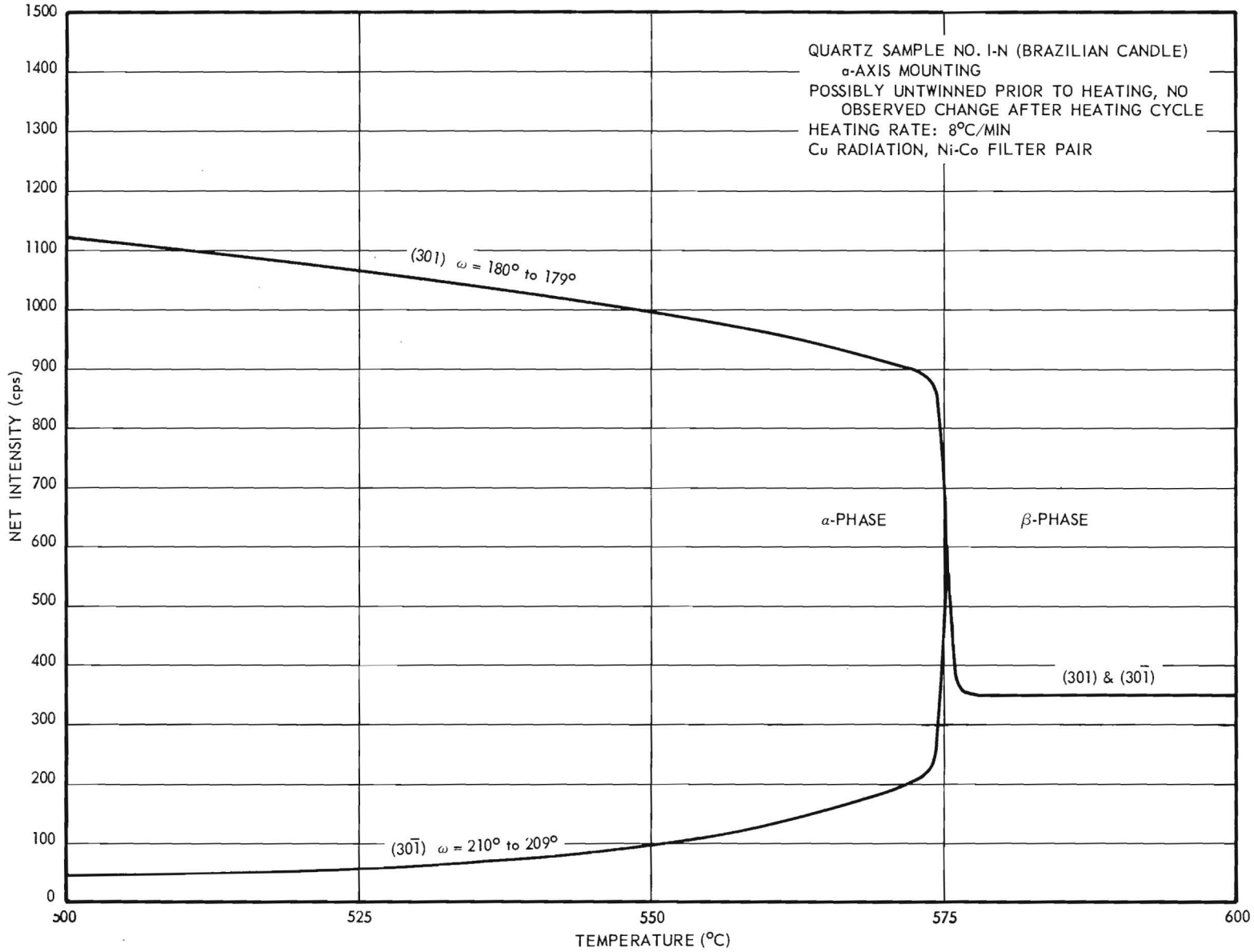


Figure 1. Temperature Dependence of (301) + (30$\bar{1}$) Intensities.

Figure 1 shows the intensities of the (301) and the $(30\bar{1})$ reflections as a function of temperature. It has been pointed out in previous reports that the ratio of these intensities to each other is particularly sensitive to Dauphiné twinning and that it would be unity if equal volumes of the crystal were allocated to each type of twin. As indicated on the figure, the optimum crystal orientation (spindle position, ω) does change by about 1 degree with temperature so that it is necessary continually to reoptimize the crystal setting as the temperature is changed. The temperature scale is not necessarily accurate but it is fairly precise, probably to within substantially less than 1° C. The actual temperature is probably about 2 to 3 degrees lower than the indicated temperature on the figure. Although the actual scatter in the data is significant, the smooth curves shown in Figure 1 are qualitatively correct.

It is the behavior of the intensities in a 3° C range from 574 to 577° C (indicated) that is particularly interesting. With increasing temperature at about 574° C (indicated) both intensities start changing rather abruptly until they both take on the same value, which value is midway between the values they had before they started the abrupt change. With continued heating there is a subsequent decrease in both intensities.

The suggested interpretation of Figure 1 is as follows. At 574° C (indicated) "tunneling" starts from one α-phase configuration to the other, until at the temperature where both intensities are the same (about 590 counts per second) equal volumes of crystal are associated with each α-phase configuration. The regions of single configuration are quite possibly of microscopic size. The atoms within each region, being still bound to vibrate within the single potential minimum associated with that phase, have vibrational amplitudes not significantly different from what they were at a 3° lower temperature. At a slightly higher temperature the atoms gain sufficient thermal vibrational energy to overcome the potential barrier between the two α-phase configurations and either (a) vibrate freely between the two α-phase potential minima or (b) vibrate with increased amplitude in a much broadened but single potential minimum centered at the midpoint between the two α-phase minima.

This interpretation qualitatively explains (a) the acquisition of a new vibrational mode at the transition which is noted in infrared studies and (b) some observers' feelings that there is an intermediate phase between the α- and β-phases; this intermediate phase would be the completely and microscopically Dauphiné twinned α-phase that occurs just prior to the true β-phase.

More observations of the occurrence and character of this "spike" in the weaker of the $(h0\ell)$ and $(h0\bar{\ell})$ intensity pair must be observed for other crystals and other reflection pairs before the above analysis can be accepted. Spikes of this type have been observed for other reflections but have not yet been subjected to the detailed review such as that above. Furthermore, calculations should be made of the intensity change expected at about 575° for (a) the increase in vibrational amplitude just described and (b) real changes in the coordinate parameters which would move the actual atomic equilibrium positions to the more special positions which in any event they do have on the average in the β-phase.

If the type of analysis indicated in connection with Figure 1 does turn out to be correct it is clear that the intensity-versus-temperature method can be a very powerful method for the study of phase transitions, particularly those displacive types which involve double configurational potential minima in the low temperature form. Many ferroelectric phase transitions, being of this type, might therefore lend themselves quite well to analyses based on the temperature dependence of Bragg intensities.

IV. FUTURE WORK

During the following quarter additional "far out" (i.e., in reciprocal space) data on both (1) relative intensities and (2) intensity-versus-temperature will be collected from milk quartz specimens.

Comparisons will be made of intensity-versus-temperature behavior for certain reflections of several crystals, including both Brazillian and other types, in addition to the milk quartz.

A monochromator is now on hand which employs the anomalously transmitted beam obtained from the Bormann effect. This beam is completely polarized and

the plane of polarization may be changed by simply rotating the monochromator without changing the direction of the anomalously transmitted beam. Therefore the monochromator is ideally suited to the application of Chandrasekhar's method for determining extinction. Thus if time permits some work will be done in employing this polarizing monochromator to determine the changes in extinction that may take place in some of the more nearly perfect crystals as the temperatures change and as the crystals are taken through the transition. These results will be preliminary because of time limitations and will probably be provocative rather than definitive if they are obtained at all.

Additional least squares refinements, carried out as a function of temperature, based on the best and most extensive data available to us will provide the principal features of the changes in thermal ellipsoid and equilibrium positions of the atoms near and at the transition temperature. The possible existence of a double configurational potential minimum in the β-phase is to be investigated by (1) least squares refinement methods, particularly by trying to place half-atoms at each presumed minimum,(2) by the use of Patterson maps and particularly the differences in Patterson maps prepared for different temperatures, (3) by the use of intensity-*versus*-temperature data, particularly by comparison of the experimental results with intensity changes at the transition calculated on the one hand from coordinate parameter changes and on the other hand from thermal parameter changes without the coordinate changes. Especially useful in (3) will be the comparison of intensity-*versus*-temperature behavior of various reflections with different values of $\frac{\sin \theta}{\lambda}$.

Final interpretations will then be made and suggestions for further work will be noted. The final report will then be prepared; it will include a section on Dauphiné twinning.

V. PERSONNEL

No personnel assignment changes have been made during the quarter.

VI. BUDGETING AND ADMINISTRATIVE MATTERS

Approximately $9,600.00 was left in the contract budget as of 30 June 1961. It is expected that these funds will be sufficient with which to conclude the project.

Respectfully submitted,

R. A. Young
Project Director

Approved:

A. L. Bennett, Chief
Physical Sciences Division

AFOSR 60-1462

TECHNICAL NOTE NO. I

PROJECT A447

COUNTER ADAPTOR AND FURNACE FOR WEISSENBERG CAMERA

by

R. A. Young

October, 1960

Contract No. AF49(638)-624
Directorate of Solid State Sciences
Air Force Office of Scientific Research, ARDC
Washington 25, D. C.

Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia

T E C H N I C A L N O T E N O. I

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Table of Contents

SEMITECHNICAL BRIEF

This "Technical Note" describes specialized apparatus built and used in connection with a study of the "Mechanism of the Phase Transition in Quartz."

The goal of the study is the determination of the detailed changes that take place in the atomic positions and atomic thermal vibrations as the quartz changes from one crystalline phase (α) to another (β) at about 573° C. The study is being carried out by the detailed examination, mathematical and otherwise, of diffracted x-ray intensities and the comparison of these observed intensities with those calculated for various possible models. To this end it is necessary to collect x-ray intensity data of high precision from single crystals and to do so as a function of temperature over a range which includes the transition temperature. The apparatus described herein (1) provides for proper and easy positioning of specimen and counter-detector so that the precision of counter detecting methods may be enjoyed, and (2) provides a particularly flexible means of heating the crystal specimens during x-ray examination.

COUNTER ADAPTOR AND FURNACE FOR WEISSENBERG CAMERA*

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ABSTRACT

A rugged and versatile counter-adaptor for a Weissenberg camera is described. It has performed well in two years of daily use which has included collection of intensity versus temperature data with conventional cold stream techniques.

Advantage has recently been taken of the adaptor design to mount, directly on the Weissenberg base, a furnace device which blows hot air along the crystal mounting axis. Crystal temperature may be held constant or easily varied over the range up to about 700° C, with no obstruction of the x-ray beams and no readjustment of the furnace position, while the entire zero layer and close-in upper layers are explored.

INTRODUCTION

The use of the counter techniques for measuring the diffracted x-ray intensities from single crystals is in a period of rapid growth. The precision with which the measurements may be made is a major reason for this growth. No less important than precision for many applications is the immediacy with which the intensity information is made available so that changes in intensity of an individual reflection may be followed as they occur.

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* Presented at "The Ninth Annual Conference on Applications of X-Ray Analysis" held in Denver, Colorado, under the sponsorship of Denver Research Institute, August 10-12, 1960.

Automatic single crystal diffractometers have been the subject of various papers[1] and are under development by at least one large manufacturer of x-ray equipment. The widely used General Electric version of the goniostat converts the standard diffractometer into a versatile, though not automatic, single crystal diffractometer. Somewhat more modest in total equipment cost are the counter-adapted Weissenberg cameras, a variety of which is in use throughout the country. While lacking versatility in comparison to the goniostat-diffractometer combination, the counter-adapted Weissenbergs do preserve the especially simple geometry of the equi-inclination Weissenberg technique. Some experiences with the North American Philips counter adaptor were reported by Peterson and Vold at the "Denver conference" 3 years ago.[2]

The counter-adaptor described herein owes some of its virtues to the designer's previous experiences with the North American Philips adaptor. It was designed particularly for use in a current broad program of studies involving the temperature dependences of Bragg intensities both below and above room temperature. After about two years of satisfactory use, both with room temperature specimens and with specimens cooled by a cold gas stream to temperatures as low as 90° K, a hot-air furnace has been added which produces specimen temperatures up to 700° C.

Since the counter-adaptor and the furnace have been used independently, they are first discussed separately.

COUNTER-ADAPTOR

Requirements

One of the design requirements was that the Weissenberg geometry was to be maintained. Therefore the Υ-axis, about which the elevation angle, Υ, (following Buerger's notation[3]) is measured, must be and remain co-axial with the Weissenberg spindle axis. The axis about which the counter azimuthal angle, ν, is measured must be perpendicular to the Υ-axis at its intersection with the equi-inclination angle or μ-axis (and the x-ray beam) and must be rotated about the Υ-axis by the amount of the Υ setting.

Various other desirable features considered in the design were as follows:

Mounting

a. The counter should be supported from either the left or right sides, at the discretion of the operator, in such manner that no forces or torques would be applied to the spindle housings.

b. The adaptor should mount with a standard shoe onto the existing cassette carriage.

Angular Motions

a. While only manual adjustment of Υ and ν were required for immediate purposes the design should provide for easy addition of a motorized drive in Υ which would not interfere with the other design requirements.

b. Both Υ and ν should be easily adjustable and readable to 0.1°.

c. The fine adjustment mechanisms in (b) should disengage to allow free motion through the full range of Υ and ν (this feature is especially important when it is necessary frequently to check the alignment of the crystal, as it is when a crystal is being taken through the first few heating or cooling cycles.)

d. The means for locking Υ and ν should be positive, easy acting, and the locking process should not measurably change the angular settings nor the counter alignment.

Rigidity

The entire adaptor should be sufficiently rigid so that normally encountered mechanical load variations, such as those transmitted through the cables to the counter and those due to normal placement of the operator's hands on any part, should not significantly change the counter position.

General Size and Disposition of Parts

a. With the left hand mounting in particular, no part of the adaptor should block the positioning of a heating or cooling air stream either coaxially with the spindle or in the front lower right area. This requirement should be met for all settings of Υ or $\nu \geq 0$ when the air stream is brought in by a 2.5 cm o.d. tube ending not more than 1-1/2 cm from the crystal.

b. The overall size, weight, and volume occupied should not be excessive and should not interfere with obtaining the full range of equi-inclination angles.

Construction

The instrument designed to meet these requirements is shown best in Figures 1 and 2. The mounting requirements are met by the shoe shown in Figure 1 and by the combination of the hollow elevation bearing, which allows the spindle housing to pass through without touching, and the "elevation axis adjustment slots." The slots are required for making the elevation axis coaxial with the spindle axis when the adaptor is changed from the left hand mounting (shown in all the Figures) to the right hand mounting. The "guide rail for bearing axis adjustment" (Figure 2) keeps the two axes parallel while the lateral adjustment is being made.

As is clear from Figure 2 a motorized drive in Υ could be added easily by the addition of a worm-drive (or a pinion-drive) ring gear on that surface of the elevation bearing assembly where the 6 screw heads are visible. The threaded block carrying the "elevation bearing clamp" is soldered to a loose fitting collar which may then be clamped to the main elevation bearing shaft by turning the "coarse adjustment" screw. Fine adjustment and locking of Υ are obtained by pushing on the threaded block with the ends of the "fine adjustment" screw, Figure 2. This arrangement has proved to be simple, convenient, and durable. The magnitude of Υ is read with the help of a vernier from the scale scribed on the elevation bearing housing.

The angle ν is read to 0.1° from the scale scribed on the carriage rail with the help of a vernier scale carried on the counter carriage. The vernier and the locking mechanism for ν are best seen in Figure 6. The lock is simply a large diameter screw which presses against the rail. The general size of the counter carriage and particularly the distance between bearing points on the rail give the counter very little opportunity to twist. One makes final adjustments of ν by placing his thumbs on the rail, on either side of the counter carriage, and rolling them to move the carriage, while at the same time being sure that both of the rear bearing members of the carriage are in contact with the rail. Perhaps surprisingly, this technique is found to be as easy to use as would be a more conventional type of screw adjustment for fine control. (This would not be the case if control to much less than 0.1° were required.)

The rigidity requirement has been met by the use of a solid hardened-aluminum rail, the counter carriage shown in the Figures, the rail bracket and brace shown in Figure 1, and a solid piece of 3/8-inch cold rolled steel angle from which to make the elevation bearing and slotted support. The diameter of the elevation bearing and the strength of its housing serve successfully to keep the actual elevation axis rigidly horizontal in spite of the torques arising from the weight of the counter and cable and from the operator's hands during adjustment of ν. End play is removed from the elevation bearing by the use of the 6 set screws shown beside the slotted-head screws in Figure 2.

The overall size and weight of the adaptor were reduced to some extent by the judicious use of aluminum and steel. As is clear from Figure 5, the counter adaptor will not in itself prevent the Weissenberg camera base from being set to any equi-inclination angle.

The hollow elevation bearing makes it possible to bring in an air stream co-axial with the spindle axis, a fact that has been taken advantage of in the furnace mounting to be described later.

The requirement for air-stream flow from the lower right is adequately met with the left hand mounting of the adaptor by use of the relatively short rail, as shown in the Figures. When the counter adaptor is mounted in the right hand position a longer rail is necessary and it is not possible to bring in the air stream from the lower right when small values of Υ are used. This has so far caused us no inconvenience, however.

FURNACE

Requirements

The furnace was designed to meet, when used on the counter-adapted Weissenberg, the following requirements among others.

a. The maximum temperature should be in excess of 600° C.

b. The temperature should be continuously and quickly adjustable (i.e., the furnace should have a small thermal lag).

c. It should be possible to maintain any desired temperature to within $\pm 5^{\circ}$ C or less.

d. The furnace should provide a region of "uniform" temperature at least 3 or 4 times as large as the specimen.

e. The various parts of the furnace and all necessary shielding should not interfere with the x-ray beams nor with positioning of the counter.

f. The furnace should not heat up the goniometer head or other parts of the x-ray instrument unduly.

g. The mounting of the furnace should be such that the position of the crystal relative to the furnace need not be changed during normal operations.

Furnace Construction

The requirements of small thermal lag (b) and no significant obstruction of the x-ray beams (e) suggested a hot-air stream furnace in which the air was heated directly from a wire heating coil. Each of the other requirements presented specific problems. The resultant device is indicated schematically in Figure 3. It consists essentially of an 18 mm Vycor tube encased in a foamed-silica and sheet-metal jacket* and containing a Kanthal wire heating coil imbedded in alumina bubbles. The alumina bubbles aid the heat transfer from wire to air, without adding appreciable thermal lag, so that exit air stream temperatures above 700° may be obtained without overheating the wire.

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*Improvements made since this paper was given incorporate a ceramic furnace tube as the outer jacket and the space between the two tubes is filled by asbestos paper. See Appendix A for a discussion of this improved version.

The thermal jacketing and the porous firebrick plug both help to reduce the lateral temperature gradient near the center of the hot-stream. The most effective single factor in producing a region of small lateral gradient is the use of the brass screens as shown in Figure 3. We are indebted to Dr. Ben Post of the Polytechnic Institute of Brooklyn for calling our attention to the obvious benefits to be derived from their use.

The stated requirements on maintaining a particular temperature are more than met through the use of a well regulated and ballasted air supply and the use of a Wheelco model 407 proportional controller operating from a regulated voltage source.

Furnace Mounting

The manner in which the remaining requirements are met depends on the mounting used. This furnace has been used successfully (1) at temperatures up to 300° C (and no doubt could have been used to higher temperatures) in conjunction with a General Electric Single Crystal Orienter (goniostat) in a standard mounting on an XRD-5 diffractometer, (2) at temperatures up to 650° C on a precession camera (precession angle 29°), and (3) at temperatures up to 700° C on the counter-adapted Weissenberg with each of two mounting arrangements.

The more interesting of these two mounting arrangements, which takes advantage of the special features of the counter adaptor just described, is

shown in Figures 4 and 6. Figure 5 gives essentially the same view of the counter-adapted Weissenberg as is given by Figure 4 but without the furnace and its accessories. Figure 6 shows furnace and counter-adapted Weissenberg in place on the x-ray machine. (Parts of a precession camera may also be seen in Figure 6.)

The goniometer and other parts of the instrument are protected from the hot air blast (See Figure 4) principally by the exhaust duct. The duct is necessarily slotted, however, to allow passage of the fiber (or in this case a ceramic rod with a quartz fiber at the end) carrying the crystal. The goniometer head is protected from hot air leaking through this slot by the aluminum foil shield placed around the crystal-bearing rod (often just crumpled and crushed into place) and by a room temperature air stream (Figure 6) which plays directly onto the goniometer head. With this arrangement the goniometer head does not become too warm to touch with the finger even when the hot-stream temperature is 700° C.*

The scintillation counter is protected from stray hot air and radiant heat (an important point when intensity versus temperature data are sought) by the aluminum foil shield shown in front of it in Figures 4 and 6.

Advantages of Mounting Shown

It is evident from Figure 4 that with this counter-adaptor and furnace combination the entire zero layer may be explored without rearrangement of the furnace. Yet the furnace may be positioned very close to the crystal (within 1 mm).

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*It has been found possible, in work carried out since the paper was first given, to enlarge the Aℓ foil shield and then to disperse with the duct in many cases.

Since the whole furnace assembly is mounted on and moves with the upper part of the Weissenberg base, the crystal-furnace relation is unchanged even when an upper level reflection is examined. With the crystal to furnace distance set at about 0.5 cm it is possible to observe, with Mok$_\alpha$ radiation, the 2nd and 3rd upper levels of a quartz crystal. This is a very convenient feature for it allows easy alignment of the crystal at operating temperatures with exactly the same heating conditions used during the collection of data.

Accessory Equipment

Certain accessories have been found to be particularly convenient.

The electrical power input to the furnace is controlled by a Wheelco model 407 controller which obtains its signal from a 3 mil chromel-alumel thermocouple approximately centered in the hot-stream but not touching the furnace.*

There has been added to the controller a specially built gear drive which moves the control point at an approximately uniform rate. This drive greatly facilitates the collection of intensity versus temperature data. Programmed controllers better for the purpose are commercially available, however.

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*Early difficulties with large apparent thermal lag, and consequent poor automatic control, were traced to the use of 6 mil thermocouple wire mounted on the furnace housing. That thermocouple was somewhat sensitive to the temperature of the housing which does indeed lag changes in the air-stream temperature.

A "thermocouple manipulator" which provides screw-controlled translations in three directions is used to position the "measuring thermocouple" in any desired relation to the specimen and as close as to within about 0.1 mm of it. This thermocouple is also made of 3 mil chromel and alumel wires. A special null indicator is used to improve the sensitivity of a standard portable thermocouple potentiometer.

PERFORMANCE OF THE HEATING SYSTEM

The power consumption of the furnace at 700° C is about 500 watts. The input air flow usually used is about one cubic foot per minute at room temperature. The life of the heating element is at least several hundred hours and is probably indefinite if the element is not accidentally overheated.

The temperature characteristics of the heating system were investigated with the help of the 3 mil measuring thermocouple. The ability of this thermocouple (and, by analogy, the control thermocouple) to follow fluctuations in air stream temperature was demonstrated by the display on a strip-chart recording potentiometer of emf output variation due to turbulence at the edges of the hot air stream.

Constancy of the air stream temperature (or at least the thermocouple junction temperature!) appears to be maintained to within about $\pm$ 1° C at 650° C with automatic control.

The distributions of temperature in cross section at 0.5 cm and 1.0 cm from the furnace are shown in Figure 7. The distributions correspond to near-maximum heating temperatures. The contour interval is 0.1 mv (chromel-alumel thermocouple) or about 2.5° C. The size of the region of near-uniform temperature is considered to be quite acceptable, especially since our specimens have usually a maximum dimension of less than 0.4 mm. Spot checking shows that, as would be expected, the region of relatively uniform temperature is at least no smaller at lower temperatures.

The dynamic performance of the system was investigated by driving the control point at about 16° C/min with the result shown in Figure 8. The deviations from a smooth curve are probably due more to weaknesses in the present control-point drive system than to any other cause. This performance is nevertheless good enough to facilitate considerably the gathering of intensity versus temperature data.

ONE APPLICATION

A study of the $\alpha \overleftrightarrow{\rightarrow} \beta$ quartz transition mechanism now in progress in this laboratory involves the collection of intensity data as a continuous function of temperature near and at the transition temperature (573° C).

The counter adaptor and furnace described are particularly well suited to these needs. The small (maximum dimension 0.2 to 0.4 mm) nearly spherical specimens are attached with Sauereisen cement to a fused quartz fiber. The

fiber in turn is attached to a 1/8-inch diameter rod which passes through the slot in the exhaust duct (Figure 4) and is held in the goniometer head. It is found to be expedient to mount the specimen within about 5° of the desired alignment. MoK_{α} radiation is generally used.

Intensity data both at particular temperatures and as a function of temperature have been successfully and relatively conveniently gathered. The capacity for heating and cooling in a reproducible fashion while the diffracted intensity is continuously recorded has been found to be quite useful.

One of the many interesting observations that have been made possible for us by this apparatus is the behavior of the intensities of the {301} reflections near the transition as is shown by Figure 9.

The behavior of the reflection labeled (301) in Figure 9 is typical for the strong members of the {301} group. The abrupt nature of the transition is clearly displayed; in fact, one may often tell when the transition has been reached by the sound the strip-chart recorder makes as it strives to keep up with the rapidly changing intensity.

Not typical of quartz but even more interesting as an example of the utility of this apparatus is the temperature dependence observed for the intensity of the $(30\bar{1})$ reflection of a particular quartz crystal. This is also shown in Figure 9. Obviously the very interesting and quite unexpected behavior of this $(30\bar{1})$ intensity at the transition and much of its behavior

on both sides would be missed with a technique which did not combine the precision of counter detection with a continually and smoothly variable specimen temperature.

CONCLUSIONS

The counter-adaptor and furnace have been used to advantage both separately and together. The temperature stability at 650° C appears to be about ± 1° C. At this temperature there is a cross-sectional region of minimum dimension greater than 1.5 mm over which the temperature is uniform to within 2° C. The particular mounting of the furnace described, made possible by a special feature of the counter-adaptor, makes it possible to examine both the isothermal relative intensities and the temperature dependence of the intensities of all reflections (with 2θ less than about 150°) in the zero and first few upper layers, and to carry out crystal alignment, over the temperature range from room temperature to 700° C without change in the crystal to furnace relationship and without obstruction of the x-ray beams.

For our purposes, at least, the counter-adaptor combines the advantages of rigidity, convenience of operation, and versatility with low cost. Redesign of the adaptor now, after 2 years use, would incorporate only minor changes. In addition to the low and high temperature applications the adaptor has been used successfully for a variety of room temperature studies. These range from crystal orientation and alignment (quickly accomplished to within less than 5' of arc) through collection of relative intensity data to studies of eqitaxial growth of thin metal films.

Use of the counter adaptor and furnace combination has, in addition to the expected results, made possible the delineation of unexpected character in the temperature dependence of diffracted intensities. Such character might be very significant in any study of temperature effects on materials.

Determination of phase transition temperatures, phase transition mechanisms, Debye temperatures, and order-disorder phenomena are among the myriad possible industrial applications of a detector and furnace combination such as the one described here.

It is our personal belief that specimen temperature variation, particularly when it can be accomplished with the continiuty and ease described here, will continue to be ever more widely used as a powerful tool for multiplying the investigatory capabilities of x-ray diffraction.

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1. See, for example:
   a. J. Ladell and K. Lowitzach, "An Automatic Linear Reciprocal Lattice Tracking Single Crystal Diffractometer," Paper G-7 at the Cornell Meeting of the American Crystallographic Association, July, 1959.
   b. K. Drenck, H. Diamant, and R. Pepinsky, "SCADAC: Single Crystal Automatic Diffractometer and Analog Computer," Paper G-8 at the Cornell Meeting of the American Crystallographic Association, July, 1959.
2. David T. Peterson and C. L. Vold, "A Counting Method for Measuring Single Crystal Diffraction Intensities Using a Weissenberg Camera," Proceedings of the 6th Annual Conference on Industrial Applications of X-Rays, Denver Research Institute, 1957, p. 181.
3. M. F. Buerger, "X-Ray Crystallography," Wiley, New York, 1942, Chapter 14.

Respectfully submitted,

R. A. Young
Project Director

Approved:

Vernon Crawford
Head, Physics Branch
Physical Sciences Division

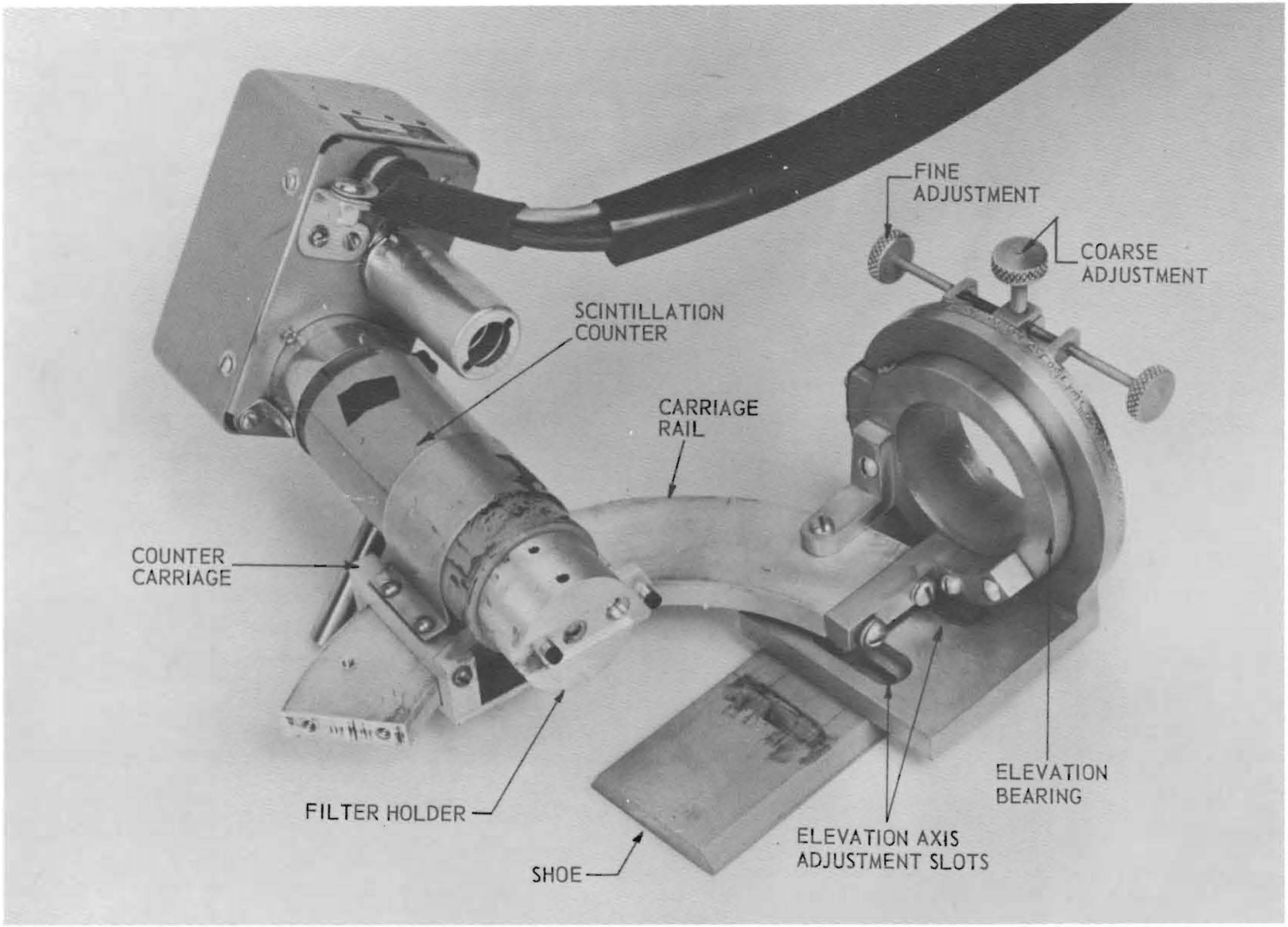

Figure 1. Counter - Adaptor.

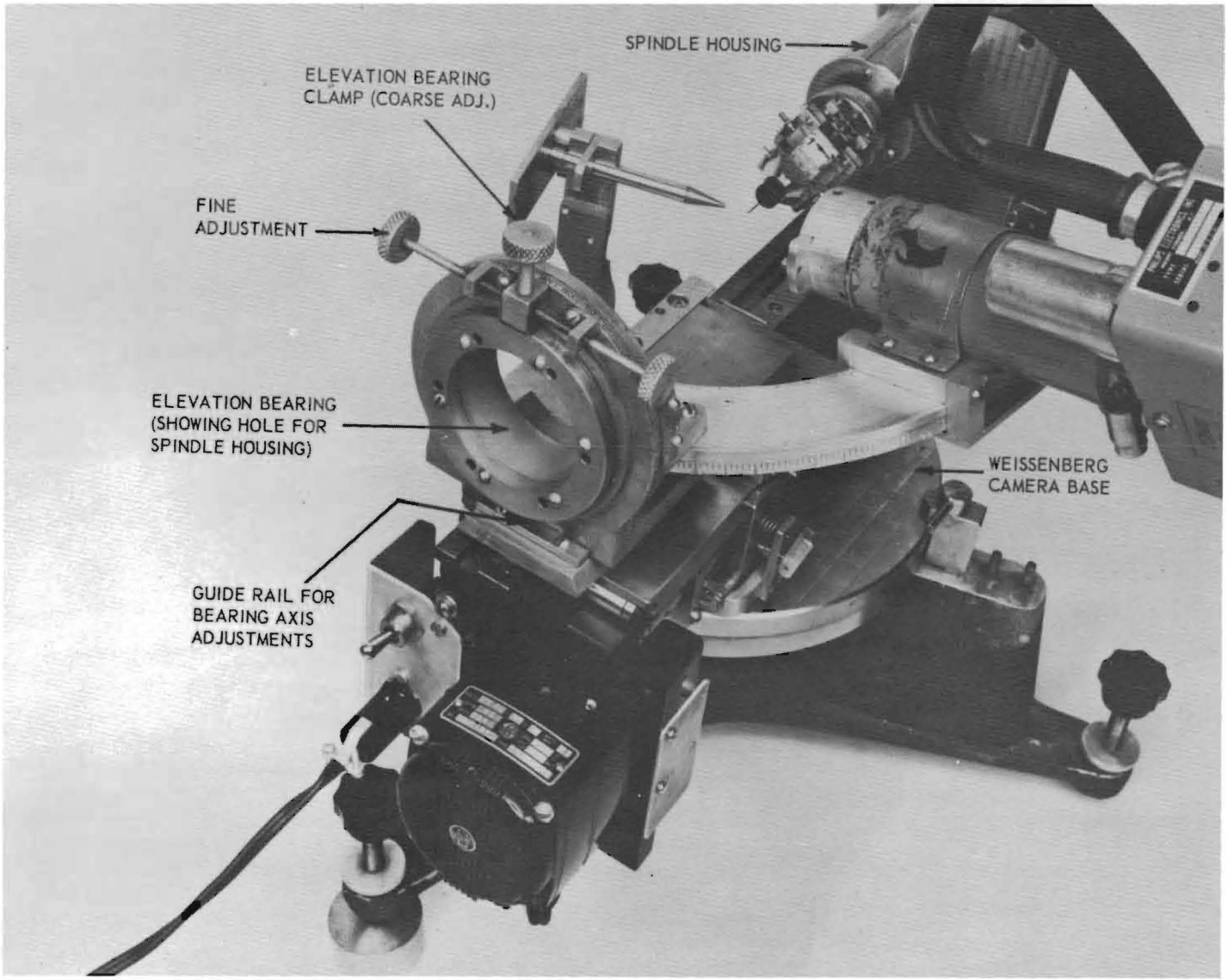

Figure 2. Counter - Adaptor on Weissenberg.

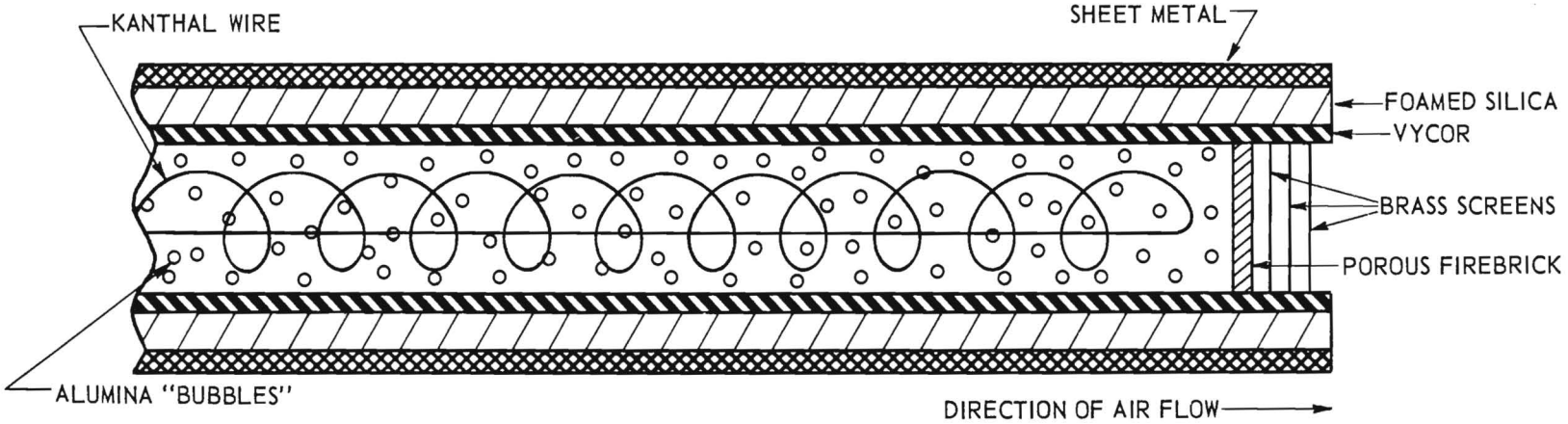

Figure 3. Hot Air Furnace.

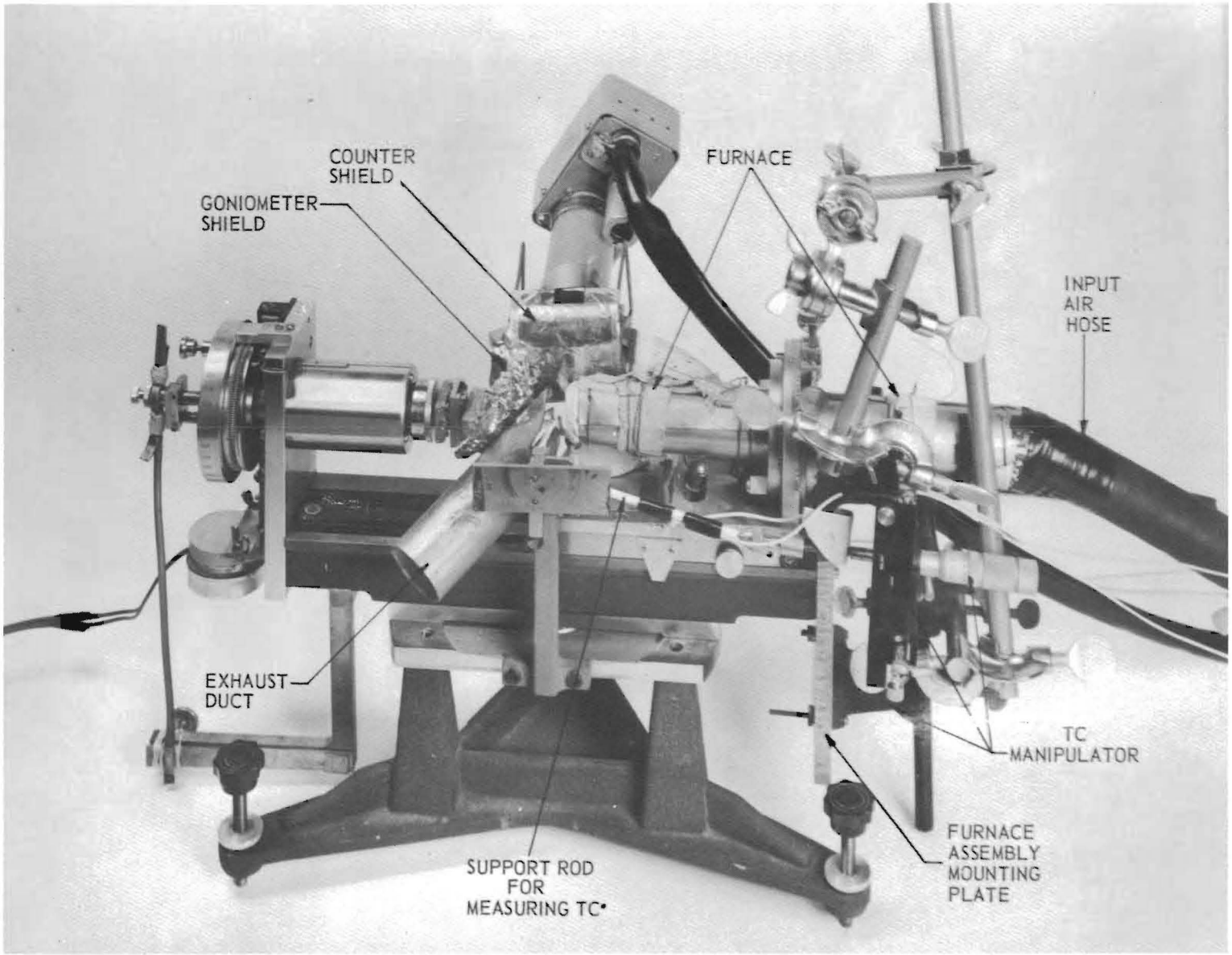

Figure 4. Counter - Adaptor and Furnace Assembly on Weissenberg.

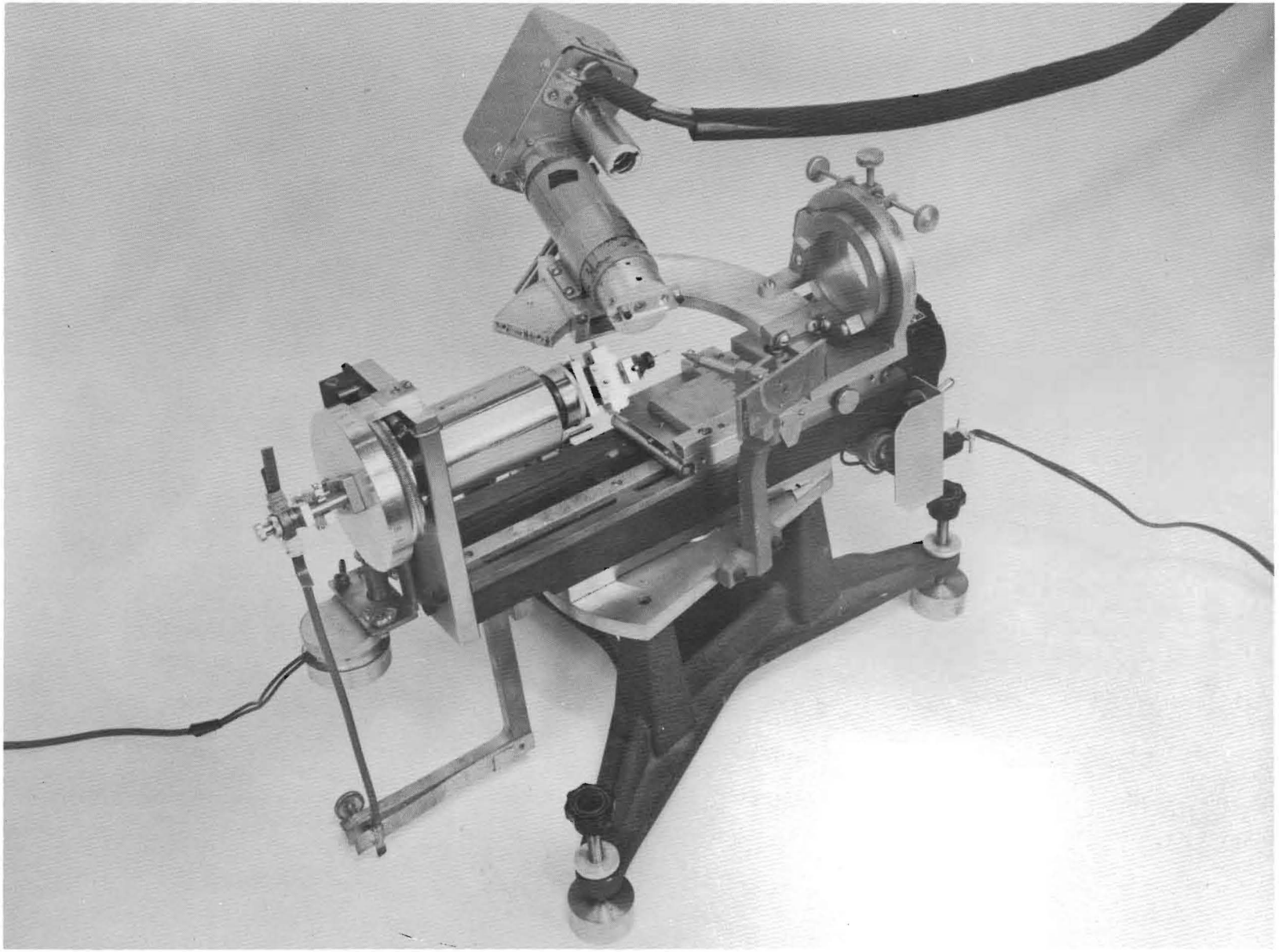

Figure 5. Counter - Adaptor on Weissenberg Without Furnace.

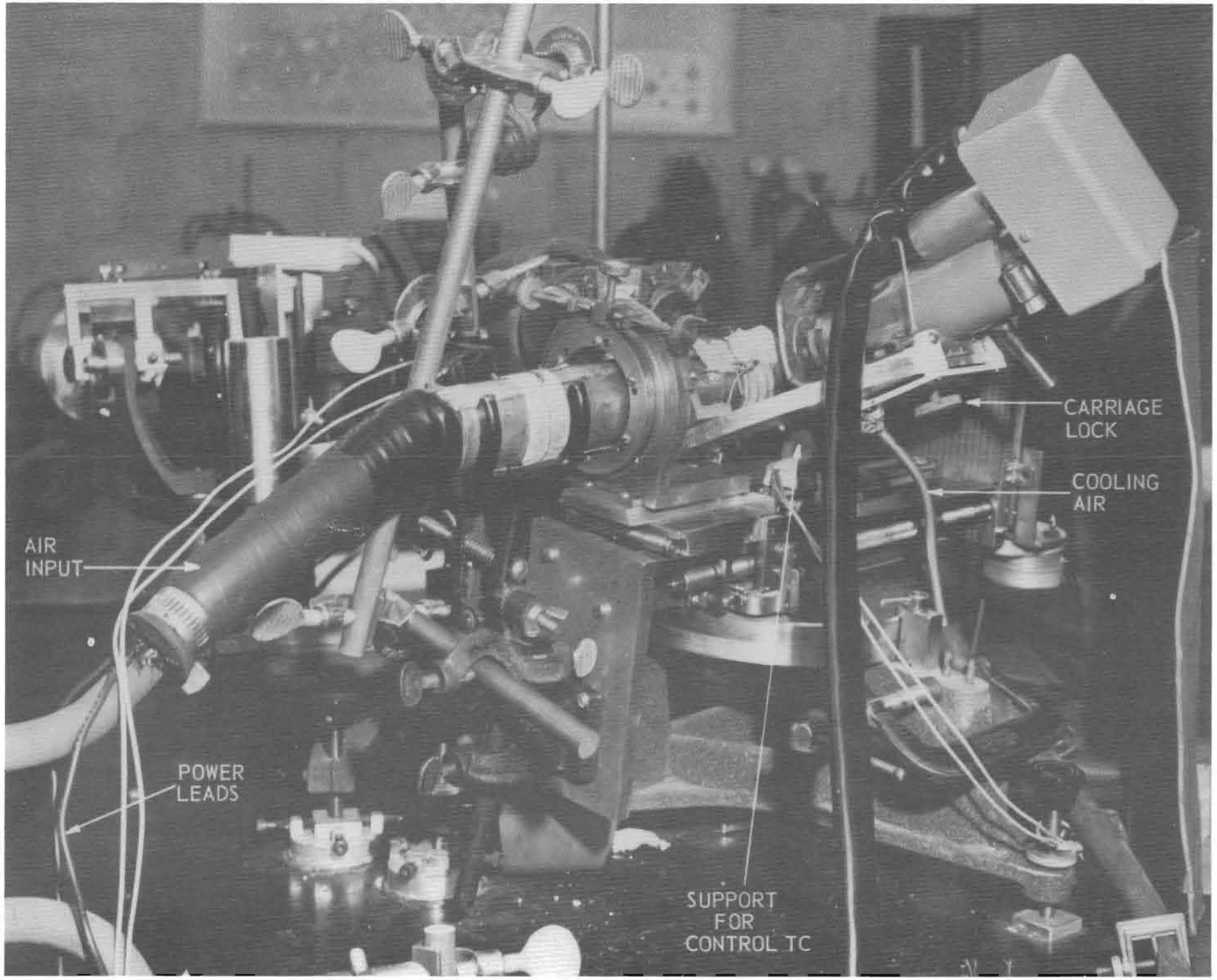

Figure 6. Counter - Adaptor and Furnace Assembly in Operating Position.

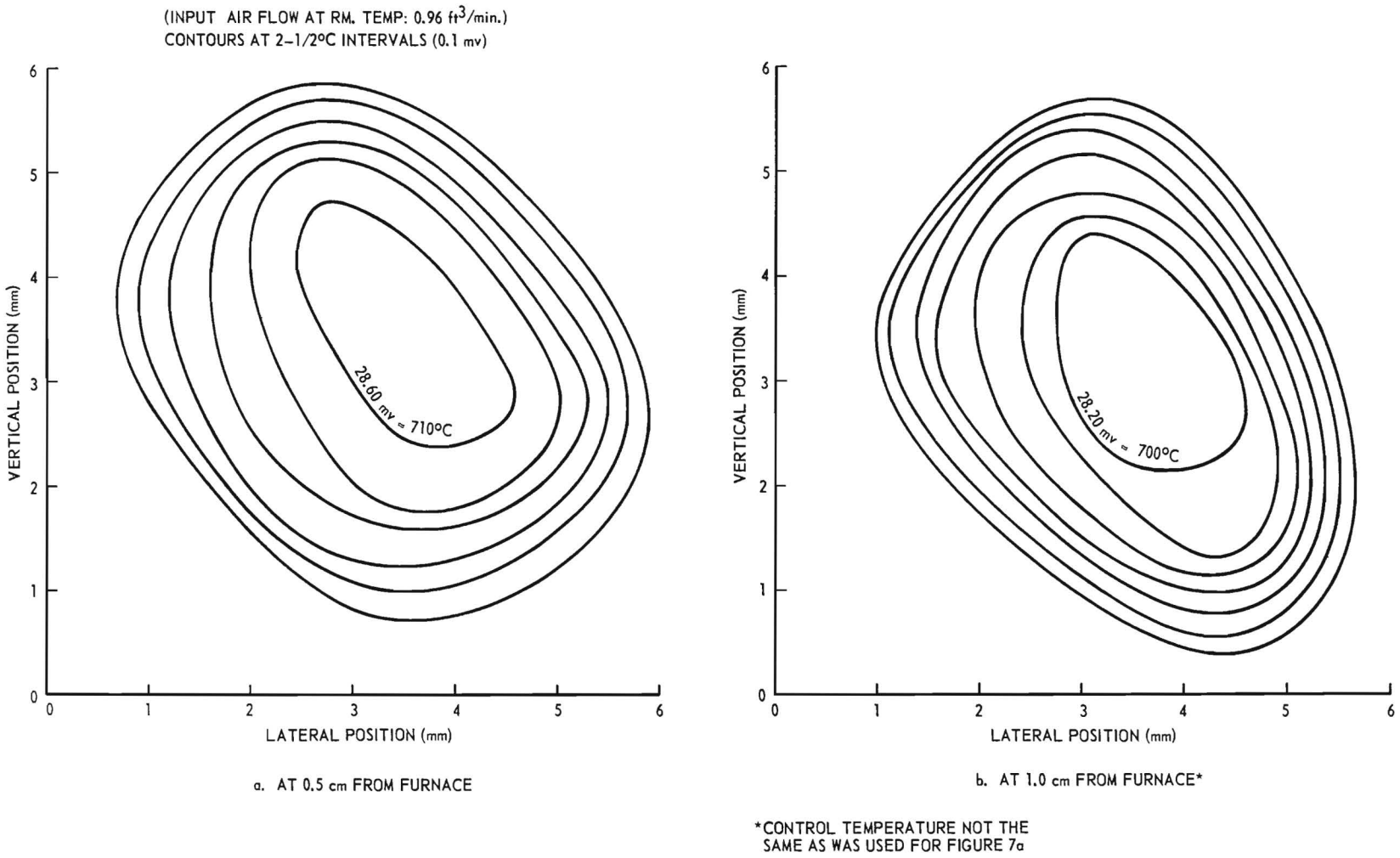

Figure 7. Temperature Distribution in Air Stream at 700°C.

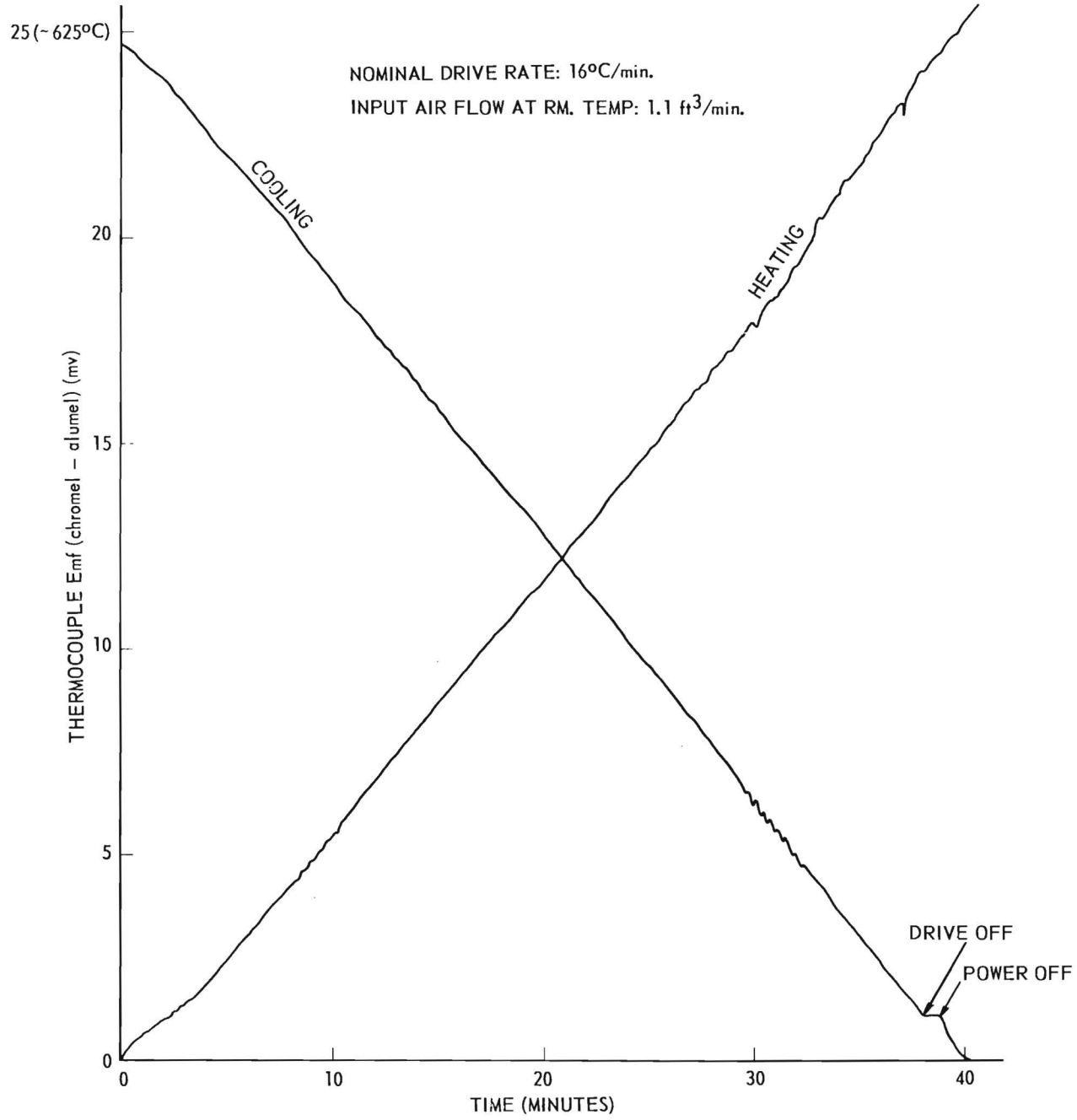

Figure 8. Dynamic Performance of Heating System.

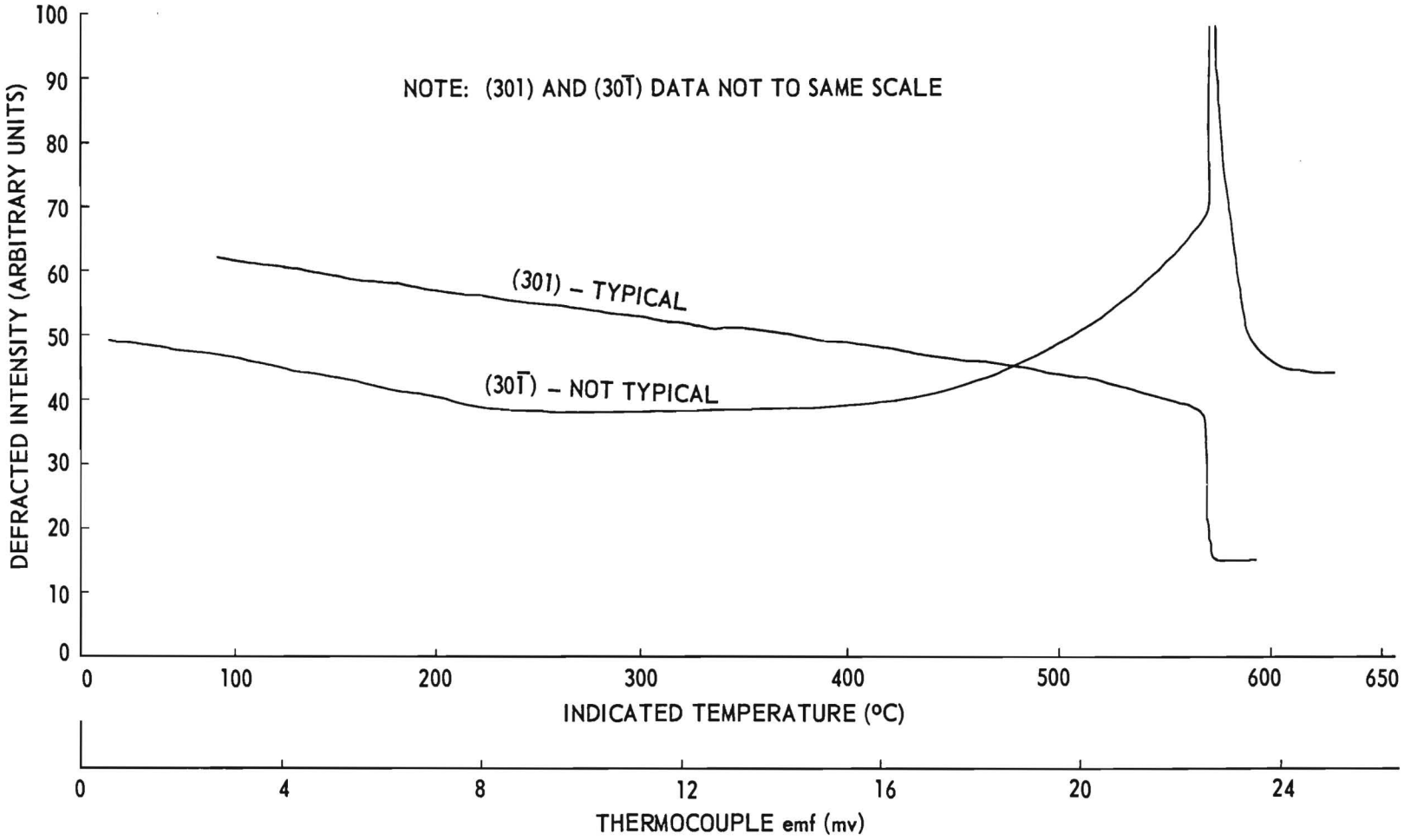

Figure 9. Observations of {301} Reflections of Quartz.

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APPENDIX A

Improved Version of Furnace and Heat Shields

Certain improvements made since this paper was first given have resulted in much more satisfactory versions of the furnace and heat shields. It seems probably that the present configurations will be modified little if at all for some time.

Improved Furnace

The whole furnace was made much neater by replacing the sheet metal jacket, Figure 3, with a ceramic furnace tube. At the same time the foamed silica was replaced by asbestos paper. The result is a neater, more substantial, and better insulated covering for the Vycor tybe.

In continued use it was found that the firebrick plug, Figure 3, became clogged, no doubt with bits of broken alumina bubbles, and that both the thermal lag and the back pressure became excessive. This was solved, apparently permanently, by replacing the firebrick plug by about 1 cm of alumina bubbles held in place by brass screens at both ends. At the same time the alumina bubbles were removed from the rest of the furnace. The result was a drastic reduction in the operating back pressure and excellent dynamic response to the controller. The dynamic response is now superior to that shown in the body of this paper. The furnace now stabilizes on automatic control at 500° C in about 3 minutes from a room temperature start.

A portion of the improved furnace may be seen in Figure A1.

Improved Heat Shields

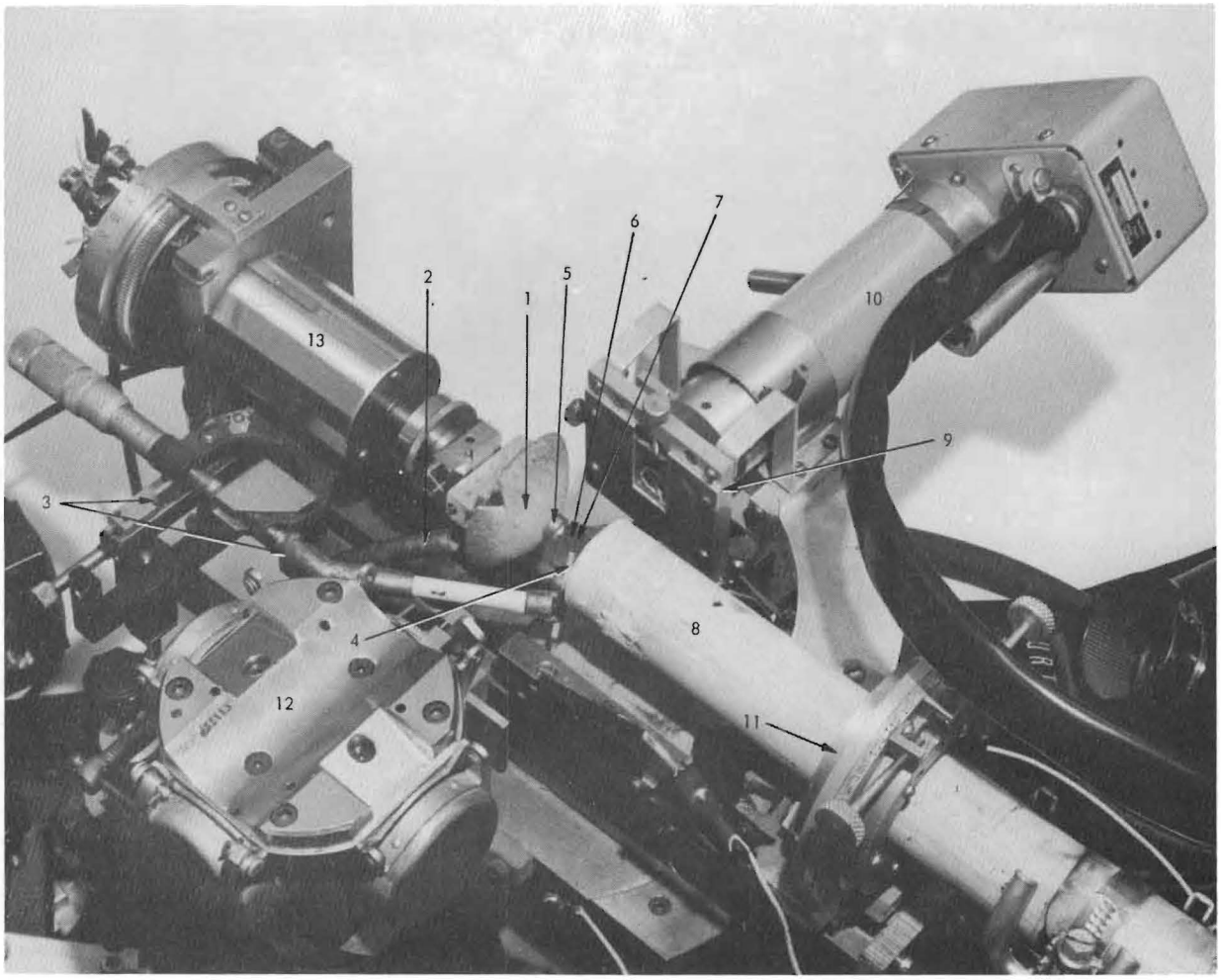
The improvements in the heat shield for the counter consisted simply of making it more rugged and incorporating in it the means for holding and centering a lead pinhole. These features may be discerned in Figure A1.

The greatest improvement made concerns the heat shield for goniometer head. It is shown in place in Figure A1 and in exploded view in Figure A2. It consists of an aluminum cap spun into the shape of a spherical section and covered with asbestos paper. The notch at one edge allows access to the inner goniometer-arc adjustment-screw. The cap is held in place by the shaft of the brass fiber-mounting plug, on which it is free to rotate (in order that the notch maybe brought to the desired position).

A cooling stream of room temperature air is played on the back of the cap with two results: (1) The goniometer head remains cool enough for one to touch with one's fingers even though the crystal temperature is 700° C and (2) all of the hot stream is drawn into the cooling stream at the back side of the cap and is discharged harmlessly in a direction away from all parts of the apparatus. Thus, no further shielding of the apparatus is required. The hot stream curls around the lower side of the cap so effectively that one may place his hand between the cap and the base of the Weissenberg without detectable discomfort--the base of the Weissenberg remains cool to the touch.

Both the furnace and the goniometer heat-shield now appear to have that desirable simplicity in design and operation which makes the whole

process of obtaining x-ray data at temperatures up to 700° C hardly noticeably different, in the experimenter's view, than collection of data at room temperature.



1. Goniometer Heat Shield
2. Room Temperature Air Stream
3. Thermocouple Manipulator
4. Thermocouple Support
5. Brass Mounting Plug
6. Fuzed Quartz Mounting Fiber
7. Quartz Crystal
8. Furnace
9. Combination Counter Heat Shield and Front Aperture Support
10. Scintillation Counter
11. Υ Scale of Counter Adaptor
12. X-ray Tube Head
13. Weissenberg Spindle Housing

Figure A1. Counter-Adaptor, Furnace, and Accessories in Place on Weissenberg Camera Base.

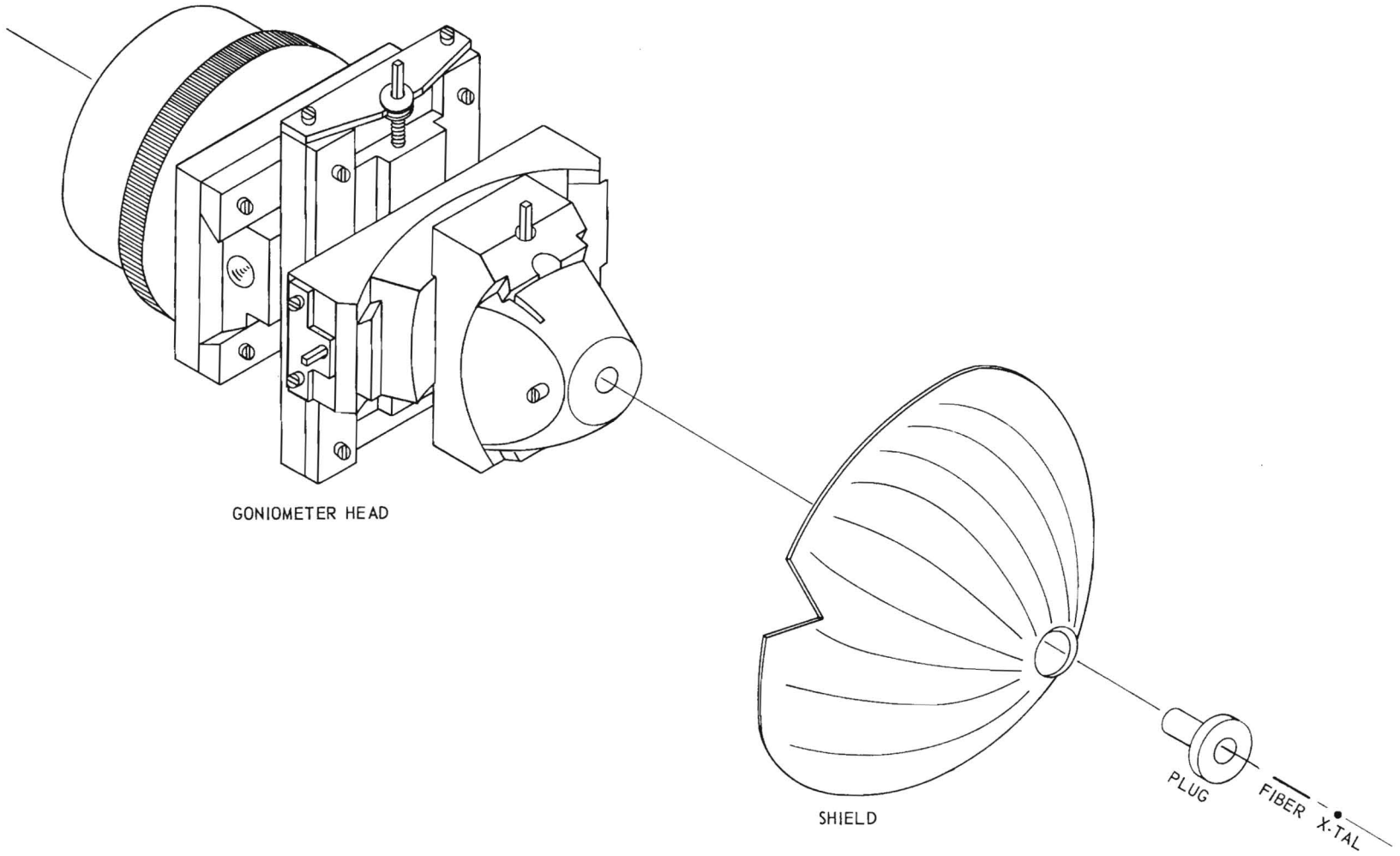


Figure A2. Exploded View of Goniometer Head and Heat Shield.